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MEASUREMENTS OF HEAT CAPACITY AND HEAT OF VAPORIZATION OF WATER IN THE RANGE 0° TO 100° C

By Nathan S. Osborne, Harold F. Stimson, and Defoe C. Ginnings

ABSTRACT

The present series of measurements of heat capacity and heat of vaporization of water in the range 0° to 100° C have been made to provide greater certainty in the values of the specific heat of water for calorimetric purposes and also to provide greater reliability in the values of enthalpy and the other derived properties for use in steam tables.

To insure the desired accuracy in the specific-heat determinations, complete new calorimetric equipment was designed and built. The same fundamental principles of fluid calorimetry by the electric-heating method were used as in previous measurements extending from 0° to 374° C. In the present case, the limited range of temperature and pressure allowed greater freedom of design to provide for higher accuracy in measurements. Heat leak was accounted for by observation, although it was kept practically nil by insulation and by thermal control of the envelope.

Temperature uniformity in the calorimeter was secured by an efficient circulation pump. Temperature uniformity in the envelope was secured by a controllable saturated-steam bath. Temperatures were measured by platinum resistance thermometers supplemented with numerous thermoelements. Heat added was measured electrically. The process of evaporation was closely controlled by manipulation of a sensitive throttle valve.

From 256 heat-capacity experiments and 152 vaporization experiments, as finally reduced and formulated, there was obtained a group of properties of water comprising specific heat, enthalpy of both liquid and vapor, heat of vaporization, and specific volume of saturated vapor in the range 0° to 100° C.

The values of specific heat have been compared with values from several important researches by both the mechanical and the electrical method. This comparison shows a more satisfactory accord of the present results with the results of Rowland, of Laby and Hercus, and of Jaeger and von Steinwehr, than with those of Callendar and Barnes.

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Part 1. A Calorimeter for Measuring the Heat Capacity and Heat of Vaporization of Water in the Range 0° to 100° C

I. INTRODUCTION

The principal purpose of the calorimeter described here was to provide for a systematic determination of the heat capacity of water from 0° to 100° C. A secondary purpose was to provide for a determination of the heat of vaporization over the same range. It was desired to obtain new experimental data on these properties to remove, if possible, some of the existing uncertainty. Of the earlier determinations of the specific heat of water, some are limited in range and the degree of accord is unsatisfactory. The measurements which have been completed, and which are described in part 2 of this report, were in part repetitions of previous measurements made in this laboratory. These previous determinations of the heat capacity of water were made for the purpose of obtaining data on the properties of saturated steam, using a calorimeter designed to operate at pressures up to 1,200 lb/in^2. While the values obtained for enthalpy of liquid water were of adequate precision for use in compiling steam tables for engineering purposes, the derived values of specific heat in the range below 100° C were not sufficiently accurate for use as calorimetric standards.

In providing apparatus for a resurvey of the heat capacity, the moderate range of pressure between 0° and 100° C allowed more freedom of design to avoid sources of experimental error. The design also provided for the determination of the heat of vaporization from 0° to 100° C. The results of these measurements are given in part 3.

II. GENERAL DESCRIPTION OF METHOD AND APPARATUS

The principles of the method used in the measurements have been described in previous publications [1],[1] and therefore are not repeated in detail in this report. This method was applied previously [2, 3] to measurements on saturated water and saturated steam from 0° to 374° C. The description given here includes mention of both the heat-capacity and the vaporization measurements.

The apparatus consists essentially of a calorimeter in which a sample of water may be so isolated from other bodies as to enable its amount, state, and energy to be accounted for. The sample may be made to pass through a chosen definite change in state while the accompanying gain or loss of energy is being determined.

A quantity of water, part liquid and part vapor, is enclosed in a metal calorimeter shell. An electric heater immersed in the water provides a means of adding measured energy to the calorimeter and its contents. Outlets with valves provide for filling and emptying the calorimeter and for withdrawing vapor. Detachable receivers suitable for weighing are connected to the outlets to hold the samples of water transferred.

For confining the energy, the calorimeter is well insulated from the influence of external sources of heat. In operation, the temperature of an enveloping shell is kept very close to that of the calorimeter shell. The small amount of heat which passes by leakage to or from the calorimeter is taken into account.

Two general types of experiments were made with this calorimetric apparatus. In the first type (heat-capacity measurements) the calorimeter with a sample of water was heated over a measured temperature range. By making some experiments with the calorimeter nearly full of liquid water and others with it nearly empty of liquid, it is possible to account for the tare heat capacity of the calorimeter, and to obtain the change of a quantity called alpha, α, which is a property of the water alone. It previously has been shown in the theory [1] that this quantity, α, differs from the enthalpy, or heat content, H, of saturated liquid water by another quantity beta, β. In other words,

$$\alpha = H - \beta.$$

The quantity β has been shown to be

$$\beta = L\frac{u}{u'-u} = Tu\frac{dP}{dT},$$

where L is the heat of vaporization, u is the specific volume of saturated liquid, u' is the specific volume of saturated vapor, T the absolute temperature, and dP/dT is the vapor-pressure derivative. In the previous experiments the quantity β was measured calorimetrically at higher temperatures, but between 0° and 100° C it is so small that its value can be calculated from liquid-volume and vapor-pressure data with greater accuracy than can be obtained by calorimetric measurements.

[1] Figures in brackets indicate the literature references at the end of this paper.

The second type of experiment (vaporization) made with this calorimeter is virtually an isothermal process. Heat is supplied to evaporate a sample of water which is withdrawn from the calorimeter at a controlled rate, collected, and weighed. From this experiment, there is obtained a value of a quantity gamma, γ, which differs from the latent heat of vaporization, L, by the same quantity, β, mentioned above. In other words,

$$\gamma = L + \beta.$$

III. APPARATUS

The essential features of this calorimeter may be explained by reference to a schematic diagram, figure 1, which shows the metal calorimeter shell, C, containing a water sample; an electric heater, H,

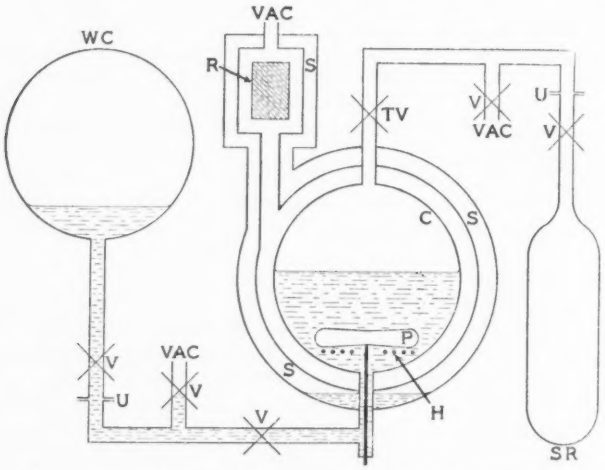

FIGURE 1.—*Schematic diagram of calorimetric apparatus.*

C, calorimeter shell; *H*, electric heater; *P*, water circulating pump; *R*, reference block; *S*, saturated steam bath; *SR*, steam receiver; *TV*, throttle valve; *U*, union; *V*, valve; *VAC*, vacuum line; *WC*, water container.

and a water-circulating pump, P. This shell is supported within an evacuated space which is surrounded by a controlled bath, S, of saturated water vapor, hereafter called the steam bath, which shields it against heat exchange with the surroundings. Provision is made for the introduction of a water sample from the water container, WC, into the calorimeter, or the withdrawal of saturated vapor through the throttle valve, TV, into the glass receiver, SR. The calorimeter and flow lines may be evacuated through lines VAC. The reference block, R, provides a temperature datum determined by a platinum resistance thermometer. Auxiliary thermoelements are used for measuring temperatures on the calorimeter shell and its surroundings, relative to this datum. The reference block is located in an inclosure surrounded by an extension of the steam bath. The calorimeter and the essential parts are shown in detail in the scale drawings, figures 2 and 3. Figure 2 shows more of the calorimeter detail, whereas figure 3 shows more of the accessory parts.

1. CALORIMETER SHELL AND INCLUDED PARTS

The purpose of the calorimeter shell shown at *C* is to hold the sample of water whose thermal properties are being determined. The shell was made nearly spherical in shape for compactness and calorimetric efficiency. It was spun from pure copper and has a thickness of about 0.55 mm. The two hemispherical ends were joined by solder,

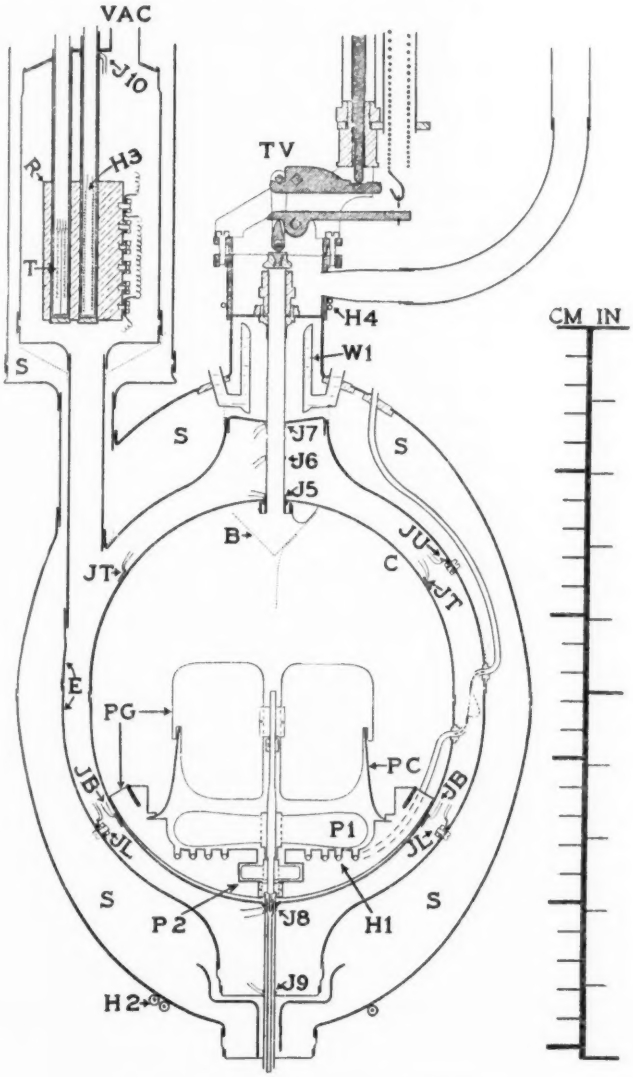

FIGURE 2.—*Scale drawing of calorimeter.*

B, baffle; *C*, calorimeter shell; *E*, envelope shell; *H1*, calorimeter heater; *H2*, steam bath heater *H3*, reference block heater; *H4*, throttle valve heater; *JT*, *J5*, etc., thermoelement principal junctions; *P1*, *P2*, pump propellers; *PC*, pump casing; *PG*, pump guides; *R*, reference block; *S*, saturated steam bath; *T*, resistance thermometer; *TV*, throttle valve; *VAC*, vacuum line; *W1*, condenser.

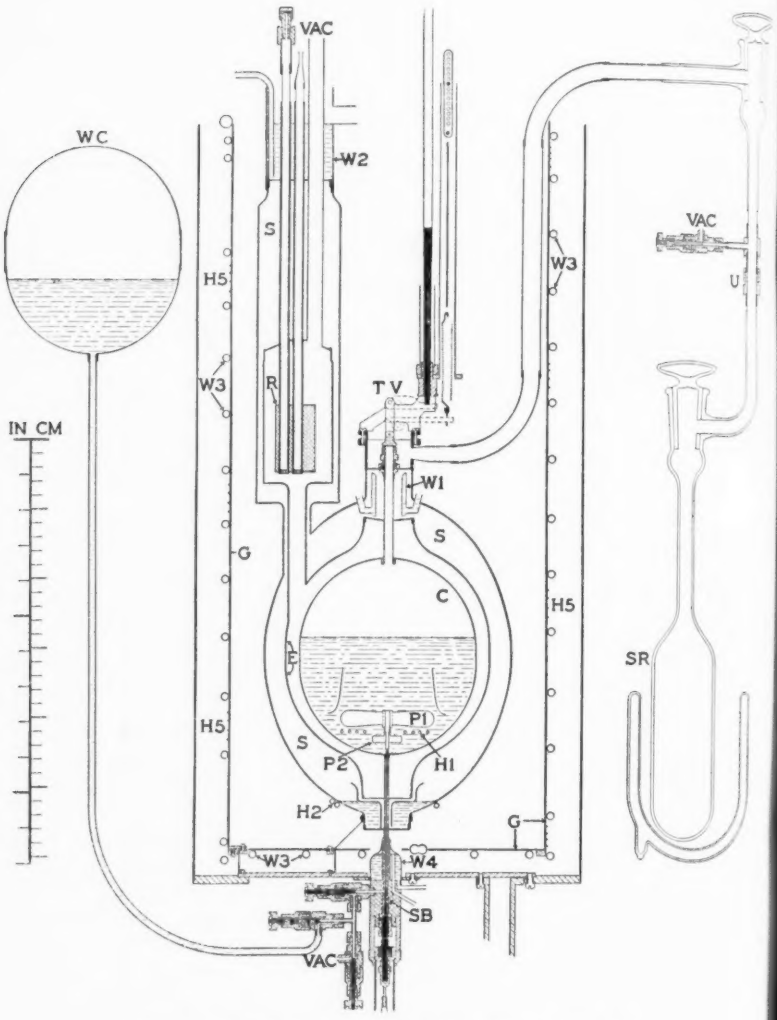

FIGURE 3.—*Scale drawing of calorimetric apparatus.*

C, calorimeter shell; *E*, envelope shell; *G*, guard; *H1*, calorimeter heater; *H2*, steam bath heater; *H5*, guard heater; *P1*, *P2*, pump propellers; *R*, reference block; *S*, saturated steam bath; *SB*, stuffing box; *SR*, steam receiver; *TV*, throttle valve; *U*, union; *VAC*, vacuum line; *W1*, condenser; *W2*, condenser; *W3*, cooling water tubes; *W4*, cooling water chamber; *WC*, water container.

with a narrow cylindrical copper band at the equatorial zone. As assembled with the various parts in place, the shell has a capacity of 1,190 cm^3.

Two tubes connected axially at the top and bottom of the calorimeter shell are designated as the "upper tube" and "lower tube", respectively. These tubes serve for the transfer of fluid to and from the calorimeter and to hold the calorimeter shell in place.

All surfaces of the calorimeter shell and the parts inside were gold-plated. The outer surface of the shell was polished to reduce heat transfer by radiation. Eight thermoelement junctions, *J*, distributed over the outer calorimeter surface were used in the evaluation of calorimeter temperature, as described later in the section "Thermometric installation."

The circulating pump consists of two screw propellers, shown at *P1* and *P2*, and a system of guides to direct flow. The larger propeller, *P1*, performed most of the work in circulating water, while the smaller propeller, *P2*, was used to avoid stagnation in the extreme bottom of the calorimeter. The specially designed blades of the larger propeller were formed from sheet copper and soldered to a hub of brass, all plated with gold and polished. The two propellers were fastened to a phosphor-bronze pump shaft, which was squared at its lower end so that it could be engaged from below by a shaft extension.

In addition to the propellers, there is a system of guides designed to direct flow and increase the pumping efficiency. The liquid water flows downward next to the inner surface of the calorimeter shell and is directed by radial guides at the bottom so that the water flows without swirl past the heater into the propellers. The water from the propeller is guided upward by a casing, *PC*, and by guide vanes *PG*, curved to remove the swirl imparted to the water by the propeller.

The pump guides form a rigid framework which supports the two pump bearings and the electric heater, *H1*. The downward thrust on the pump shaft is taken on a copper-nickel washer located just below the small propeller, *P2*. This whole pump framework is held down against the calorimeter shell by a threaded connection to a short piece of the lower outlet tube which extends into the calorimeter.

The electric heater shown at *H1* is an insulated resistor encased in a coiled metal tube sealed hermetically through the shell. It consists of about 107 ohms of a chromium-nickel-alloy wire, 0.2 mm in diameter with 0.4-mm copper leads. This resistor was wound in helical form, 0.6-mm outside diameter, and embedded in magnesia for insulation. The resistor with leads was sheathed in a copper tube drawn down tightly on the magnesia to an outside diameter of about 2 mm. This sheathed resistor was then bent to form a flat spiral of five turns, the largest being 6 cm in diameter. This coil was fastened in slots in the metal guides just below the large circulating pump propeller, *P1*. The resistor is so located as to concentrate the heating in the region just below the large propeller. The leads extending out from the envelope shell, both for current and potential connections, were made like the leads of the sheathed resistor.

For measuring the potential drop in the calorimeter heater, two potential leads were joined to the current leads where they cross the vacuum space between the calorimeter shell and the envelope. These junctions were located to include in the measured electric-energy input that part of the heat developed in the leads, which went to the calorim-

eter. Choice of suitable proportions of the leads in this boundary region of the calorimeter was a compromise between thermal conductance, electrical resistance, and convenient battery voltage. As made, the two current leads contributed but little to the total heat-leak transfer, and their combined electrical resistance was only 1/3000 of the calorimeter heater resistance of 107 ohms. Therefore, only 1/3000 of the energy input was developed in the current leads between the calorimeter and envelope shells, and so a small inequality in the eventual distribution of this extraneous heat was negligible.

To minimize the uncertainty of the accounting for the heat developed in this small resistance, the current leads, their insulation, and their sheaths were all made as much alike as possible on both sides of the vacuum space. The sheaths were soldered into the shells similarly, and the leads extended about 3 mm beyond their sheaths. In this way, the two electric connecting links had equal thermal connection with the calorimeter and the envelope shells. The current links were made of 0.3-mm gold wire about 4 cm long. One potential lead was connected to the calorimeter end of one link. The other potential lead was connected to the envelope end of the other link. In this way, the electric power developed in one link was apportioned to the calorimeter, and the power developed in the other link was apportioned to the envelope. Thus it was not necessary to connect potential leads within the vacuum space to the midpoints of the links, where the temperature of the wire rose above the calorimeter temperature during the heating period. These potential leads were made small and long to keep their thermal conductance negligible.

In order to prevent passage of liquid drops during the vapor withdrawal experiments, a baffle, *B*, shown in figure 2, made of conical-shaped wire gauze, was installed near the vapor outlet tube.

2. THERMAL-PROTECTING ENCLOSURE

In an ideal calorimeter no unmeasured heat would be gained or lost. This ideal may be approached by three means: First, the calorimeter may be thermally insulated from its surroundings. Second, the surroundings may be kept approximately at the temperature of the calorimeter. Third, the heat transferred may be accounted for by observation. In the present calorimeter, all three means were provided by use of a protecting enclosure for the calorimeter. This thermal-protecting enclosure will next be described.

The enclosure which surrounds the calorimeter is used to control heat leak to or from the calorimeter and to provide for determining the correction for the small unavoidable heat leak. The inner wall of the enclosure is a shell called the envelope, shown at *E*. It is a closed copper shell made in the same manner as the calorimeter shell, but larger. At the bottom of the envelope, the seal to the lower tube was made with a thin copper disk to accommodate differential expansion. The copper envelope shell is 0.55 mm thick, gold-plated and the inside surface polished to reduce heat transfer by radiation to the calorimeter. The space between the calorimeter shell and the envelope was evacuated for improving the insulation, leaving radiation between the polished gold surfaces as the chief path for heat leak. In the preliminary cooling of the calorimeter, this space was filled with helium to promote heat removal. Eight thermoelements on the inner surface of the envelope are used in the control and evaluation of

heat leak, as described later. To provide a space for the reference block, *R*, described later, an extension to the envelope is located as shown.

Control of the envelope temperature is an important factor in the operation of the calorimetric equipment. Upon this control depends not only the magnitude of the heat leak, but also its correct evaluation. In the calorimetric measurement, it is important that the envelope temperature be kept uniform and close to the average temperature of the calorimeter, not only when at the initial and final steady states, but also during the heating period. Another function of the envelope is the cooling of the calorimeter as a preliminary to a series of measurements. In consideration of the several functions of the envelope, a saturated-steam bath was chosen to control its temperature. An electric heater for vaporizing water and water-cooled condensers furnished the means for controlling the steam bath. The saturated steam furnished the medium for distribution of heat or refrigeration to the parts of the envelope, and thus automatically provided the desired uniformity of temperature distribution and the desired responsiveness in temperature regulation.

The saturated-steam bath, *S*, occupies the space between the envelope and a third shell of brass. This shell, or steam jacket, as it is called, is entirely closed except for small tubes for introducing or removing liquid water and vapor. A flexible copper disk was used to join the brass shell to the axial lower tube. The volume of this steam space between the steam jacket and the envelope was about 2,000 cm^3. The sheathed heater, *H2*, soldered to the outside of the steam jacket just below the level of the pool of water inside, furnished the controlled source of heat input. The vapor spaces were sufficiently open so that only negligible pressure differences could exist, even when there was flow of vapor to the remote parts.

The action of this vapor bath depends upon the latent heat of the water vapor and upon the principle that the temperature of a wet surface is determined by the vapor pressure. It therefore follows that the temperature of the entire envelope responds to any increase in saturation temperature of the vapor. In other words, the saturated steam acts as an automatic thermodynamic distributor of heat and equalizer of temperature for the space which it occupies. In heating, the saturation temperature of the vapor is raised above that of the metal, and condensation takes place, using up the latent heat of the vapor to add heat. The heat flows to the shells through whatever condensed liquid is on the metal. Gravity tends to make the condensed water run down to the pool at the bottom, where it receives heat and goes through the cycle again. Since the entire mass of fluid in this space is small and the metals of the envelope and jacket are thin, the temperature of the envelope is quickly responsive to changes in power imparted to the heater.

For the purpose of initial cooling preliminary to a day's experiments, or for a steady heat drain to be compensated by heat for regulation, two condensers are provided in the steam bath, as shown at *W1* and *W2*. Cooling was supplied to these condensers by water, regulated in flow and temperature. The water condensed within the steam bath was directed by wire-gauze leaders to parts which needed to be kept wet. The surplus returned by gravity to the pool at the bottom.

It is possible that the surfaces are not always completely wetted,

but even so, large temperature gradients could not be produced in the well-conducting envelope shell. The steam-bath enclosure was found to have a very small air leak, which made it necessary to purge it of air occasionally to secure the best operation. This was done by drawing off a small amount of steam from the region of the condenser, *W2*.

In order to protect the steam bath from the influence of the outside temperature, it was surrounded except at the top by a controlled metal casing called the "guard", shown at *G* in figure 3. This guard was a sheet-copper cylinder with a plane bottom. It could be cooled by means of a system of cooling-water tubes, *W3*, distributed over its surface. Heat could be supplied by an electric heater, *H5*, distributed over the surface. By thus controlling the temperature of the guard, the operation of the steam bath was improved.

Outside the guard there is another shell made of aluminum, for a cover. For the purpose of insulation, the blank spaces inside the cover and the guard were filled with insulating material consisting of wool and kapok.

3. CONNECTIONS TO THE CALORIMETER

The calorimeter shell is held in place by two tubes of copper-nickel alloy. In addition to furnishing a firm support for the shell without too great heat conduction, these tubes serve also for the transfer of fluid to or from the calorimeter. The "upper tube," which has an outside diameter of 6.35 mm and a wall thickness of 0.25 mm, connects to the vapor throttle valve, *TV*, which permits control of the rate of flow of outgoing steam in the evaporation type of experiments. The diameter of this upper tube was large enough to allow for adequate rates of withdrawal of steam at the lower temperatures. Near 0° C, where the specific volume of saturated steam is over 200,000 cm^3/g, it was possible to withdraw about 0.63 g/min.

During the heat-capacity experiments, which preceded the vaporization measurements, the upper tube was sealed at both the bottom and top by disks across the ends. This was to exclude water which might distill from end to end and thereby transfer unmeasured heat. These disks were removed prior to the vaporization experiments.

The "lower tube", which has an outside diameter of 3.0 mm and wall thickness of 0.35 mm, encloses the propeller drive shaft of the circulating pump. It also connects to the valve through which the calorimeter is filled or emptied.

The container, *WC*, for storing and transferring water samples was a copper shell similar to but slightly larger than the calorimeter shell, tinned on the inside to avoid contamination of the water sample, and with a tubular stem ending in a valve. It was connected to the calorimeter by a union. The long stem was to give head for running the water in or out when the vapor pressure was low.

4. STUFFING BOX AND PUMP DRIVE

The calorimeter circulating pump is driven from a 1/75-hp synchronous motor, using controlled-frequency alternating current to provide a constant speed. The drive is transmitted through a speed-reducing gear train to a vertical shaft running in a stuffing box below the calorimeter. From this shaft, a tubular extension with squared

ends transmits the rotation to the bottom of the calorimeter pump shaft.

The stuffing box, shown at *SB* in figure 3, was taken from an older calorimeter and has been more fully described in a previous publication [2]. The shaft through this stuffing box is of hardened tool steel 1 mm in diameter where it runs in the packing. A packing material of soft kid leather impregnated with a mixture of paraffin and vaseline was found to be satisfactory. This packing is kept compressed to the proper tightness around the shaft by a spring acting between the retaining ring and the threaded cap. Clearances were made small to avoid exuding the packing. The agreement of the amounts of water put in and taken out of the calorimeter was a check on the satisfactory tightness of the stuffing box.

The stuffing box was cooled with water circulating in a chamber, *W*, around the shaft tube at the top of the stuffing box. In experiments at temperatures near 0° C, this cooling was found necessary to prevent transfer of unmeasured heat to the calorimeter by boiling in the lower tube, whereas in experiments at higher temperatures, it was necessary to keep the packing cool to prevent leaking.

5. VAPOR LINE AND THROTTLE VALVE

The vapor throttle valve used in the vaporization experiments is an extremely vital part. On it depends the precision with which the experimental process of evaporation can be controlled. The valve opening must necessarily be large enough to allow sufficient flow of vapor when the specific volume is large at temperatures near 0° C. It should also be capable of closing tightly in order to permit accurate accounting for mass and energy. It should also allow steady, continuous adjustment, so that the evaporation temperatures can be controlled by regulating the flow.

The vapor throttle valve is shown at *TV*. It is made as a cylindrical cell joined to the top of the steam jacket, capped by a flexible corrugated-copper diaphragm, clamped tightly to the upper rim of the cell. This diaphragm seals against the atmosphere and carries a short valve stem at the center. The stem projects above and below the diaphragm, to which it is sealed by hard solder. The flexibility of the diaphragm permits about 1-mm linear motion of the stem to open or close the flow aperture. The outflow tube ends in a brass plug, which forms the seat. The actual seat (6.1-mm diameter) is merely a 45° sloped ridge rising about 0.15 mm above the plane end of the brass plug. The part of the stem which bears on the seat has a flat face and is fastened to the diaphragm with a threaded stud. The stem face was covered with a thin film of soft rubber, applied by dipping in latex and vulcanizing. The performance of this soft-rubber coating exceeded all expectations. It enabled the valve to be closed tightly with no perceptible leak and permitted fine regulation of throttling. One application of rubber served for the entire series of evaporation experiments.

The valve stem is operated by two levers acting axially on the stem outside the diaphragm. One lever thrusts a strut against the stem to close the valve, and the other lifts it by a stirrup to open the valve. These levers act on knife-edges to avoid any irregularity in their motion. The closing lever is actuated by a spring which not only removes any backlash but keeps a steady moderate force against the

seat of the valve when closed. The opening lever with a mechanical reduction of motion of 4 to 1 is operated by a screw with a pitch of 32 threads per inch. The shaft of this screw extends up to a grooved pulley above the calorimeter and is driven by remote control with a wire belt from a small pulley over the observing bench. A shaft from this pulley extends down to a handwheel and lever easily accessible to the operator. Using an additional lever 20 cm long, which could be clamped to the handwheel, there was a total reduction of motion of over 30,000 to 1 from the end of this lever to the valve stem. In spite of this large reduction, there was no detectable backlash in the operation of the valve. The nicety of the mechanical operation of the throttle, and the consequent excellent control of evaporation conditions amply repaid for the effort expended on the refinement of this throttle valve.

A sheathed heater, shown at *H4* in figure 2, was soldered to the body of the throttle valve to maintain both the valve and the upper tube warmer than the calorimeter. This was to prevent water from condensing in the upper tube during the evaporation experiments.

The outlet tube from the throttle was made larger than the inlet to accommodate the larger specific volume of vapor after throttling. The vapor line from the throttle to the receiver is nowhere less than 1 cm in diameter. The vapor line extends up and out of the guard space, through copper and copper-nickel tubes to a glass stopcock. Beyond the stopcock, a union, *U*, provides for the attachment of either of two Pyrex-glass containers for collecting the samples of vapor by condensation in liquid air. A side tube with valve permits evacuation of the vapor line. The glass containers, of about 225-cm^3 capacity, are provided with unions and stopcocks so that they can be detached and weighed for determining the amounts of samples.

6. THERMOMETRIC INSTALLATION

Platinum resistance thermometers and thermoelements were used in the control and measurement of temperature in this apparatus. A resistance thermometer, *T*, placed in the copper reference block, *R*, determines a reference datum on the International Temperature Scale, from which small temperature differences to the calorimeter or other points are measured by means of thermoelements. Thermoelements were also used differentially for the survey of temperature distribution and for regulation of the calorimetric processes.

The reference block, *R*, is located in a space somewhat apart from the calorimeter to avoid direct interchange of heat but is connected to it through a tube for evacuation and for installing differential thermoelement wires. The surrounding steam jacket maintains the temperature of the enclosure approximately at the temperature of the calorimeter. The reference block was designed to give adequate thermal connection between the resistance thermometer and the reference junctions of the thermoelements. It is of copper in the form of a right hexagonal prism, 5 cm tall, with three broad vertical faces on which the reference junctions of the thermoelements and attachments for the leads are located. These attachments are for intercepting heat conducted along the leads and will be referred to as "thermal tie downs."

Four vertical round holes in the reference block are the sockets into which fit the several tubes containing resistance thermometers

and the tube containing an electric heater, *H3*. The heater socket is at the axis and the thermometer sockets are located symmetrically. Tubes of thermally resistant Cu–Ni alloy extend up from these four sockets successively through the envelope, the steam space, the outer wall of the steam jacket, and the water in the condenser, *W2* in figure 3, to the outside. A length of 4.5 cm was allowed in the vacuum space to give thermal separation from the envelope and a length of 12 cm in the steam space permitted a resistance thermometer coil to be placed there for automatic regulation of the steam-bath temperature.

The platinum resistance thermometer used as a working standard for the temperature measurement was of the four-lead potential-terminal type described by C. H. Meyers [4]. The windings were of pure platinum wound on a mica cross, and the initial strains were relieved by annealing the completed thermometer at 660° C. The thermometer was then sealed in an atmosphere of helium in a tubular sheath of copper-nickel, 6.3-mm in diameter and 46 cm long. The calibration was made according to the specifications for the International Temperature Scale [5], using the fixed points of ice, steam, and boiling sulphur as 0°, 100°, and 444.6° C, respectively. The thermometer fulfilled the requirements of the specifications for the International Temperature Scale and was recalibrated several times during the calorimetric experiments.

There are, in all, 22 thermoelements within the vacuum space, all having their reference junctions on the reference block. Some of the thermoelement principal measuring junctions are shown at points labeled *J* in figure 2. Eight of these thermoelements have their principal junctions uniformly spaced on the outer surface of the calorimeter so as to evaluate the average temperature. Four of these on the bottom hemisphere are connected in series and designated as *JB*. The other four on the top hemisphere, which have separate leads to allow for examining temperature uniformity in azimuth, are also connected in series and designated as *JT*. All eight in series may be used to refer the average temperature of the calorimeter to the reference block, i. e., to the standard thermometer. Similarly, eight principal junctions on the inside surface of the envelope evaluate its average surface temperature; four of these on the lower part are designated as *JL*, and four on the upper part as *JU*. All eight on the envelope may be opposed to the eight on the calorimeter for heat-leak control and measurement.

In addition to the 16 thermoelement junctions located on the surfaces of the calorimeter and envelope shells, there are five more located on the connecting tubes between the shells. These thermoelements are used in the control and measurement of heat leak by metallic conduction along the tubes. The three principal junctions on the "upper tube" are shown at *J5*, *J6*, and *J7*. Junction *J6*, located midway between *J5* and *J7*, was used for determining the temperature of the steam withdrawn in the evaporation experiments. The two junctions on the "lower tube" are shown at *J8* and *J9*.

One thermoelement, shown at *J10*, is placed near where the tubes from the reference block pass through its envelope. This thermoelement is useful as a detector or purge indicator, since it quickly shows local temperature differences when enough air eventually leaks into the steam jacket to interfere with the free transfer of heat by the steam. For the purpose of regulating the temperature of the guard

shell, one thermoelement was placed near the top of the guard. During the evaporation experiments, a thermoelement was used on the outside of the throttle valve for regulating the heat applied.

The thermoelements used in this apparatus were made of No. 32 (0.20-mm) Chromel *P* wire containing about 90 percent of Ni and 10 percent of Cr, and No. 34 (0.16-mm) constantan wire containing about 60 percent of Cu and 40 percent of Ni. These wires, which gave about 60 μv°C for single elements, were insulated with silk and covered with Glyptal lacquer. The junctions of these elements were made in three different ways, depending on the way the thermal contact had to be made to acquire the temperature of the surface where they were placed.

The usual type of junction was on a copper terminal made in the form of a narrow washer with a radial tag to which the wires were soldered with the least bit of solder. These terminals were clamped with a screw stud and nut between thin mica washers to the metal whose temperature they were to acquire. They were somewhat larger but made according to the same principles as those described in previous reports [2, 3]. These terminals were used on the reference block for the "reference junctions" and for the first "tie-downs," and for the eight principal junctions on the envelope shell.

A second type of junction, used on the outside of the calorimeter shell, was made by soldering the two wires to larger plates of copper. These plates were insulated with thin sheets of mica and lacquer and held down with two narrow thin bands of copper extending around the shell in great circles.

The third type of attachment was used on the tubes between the calorimeter and envelope shells. In this type, the two wires were soldered together end to end, reinsulated with silk, and bound and lacquered to the tube for several turns away from the junction to insure that the junction was at the temperature of the tube.

Each thermoelement had two reference junctions on the reference block, although in cases where the elements were connected in series, some of the reference junctions were common to several elements. Eighteen copper leads from reference junctions sufficed for all of the temperature exploration it was desired to make. Their leads were carried in coils from the reference junction terminals near the bottom of the reference block to "thermal tie-downs" with similar terminals near the top of the block. From these tie-down terminals, the wires led up through a flat copper-nickel sheath which extended through the steam jacket to above the liquid in the condenser. These silk-insulated wires were in a single layer and sealed into the flat copper-nickel sheath with Glyptal for electric insulation and thermal contact. The length in thermal contact with steam sufficed to bring the temperature of the wire at the envelope boundary very close to the steam temperature. The tie-downs on the upper part of the reference block still further eliminated any temperature gradients on the lead wires toward the reference junctions.

Various combinations of the thermoelements for the several functions mentioned above were provided for by connections to specially built all-copper distributing switches. By manipulation of these switches, the observer could quickly shift from one to another combination, with little more delay than for galvanometer response.

The electromotive forces of the thermoelements were measured on a Wolff potentiometer designed by F. Wenner. The potentiometer

measurements were referred to a standard cell, described in part 2 under "Accounting for energy." The electromotive forces measured were so small that the potentiometer calibration errors were negligible.

The eight thermoelements used to measure the temperature of the calorimeter and contents were calibrated in place against the resistance thermometer in the reference block. This calibration procedure was first to observe the resistance thermometer and thermoelements, when the reference-block temperature was very close to that of the calorimeter. The reference block was then heated for a few seconds, keeping the calorimeter temperature constant, and the thermometer and thermoelements observed again. The change in the electromotive force of the thermoelements was then given directly in terms of the change in temperature by the resistance thermometer. No evidence was found that the calibration of any of the other thermoelements differed at all from this one and furthermore, even moderate differences could have had no significant effect on the results.

The resistance of the thermometer was measured with a Mueller bridge [6] built by O. Wolff and calibrated several times during the experiments. The addition of a commutator with normal (N) and reverse (R) positions adapts the bridge for measuring the resistance between the branch points of a four-terminal resistance thermometer. A bridge current of 5 ma was used, half of which passed through the resistance thermometer. The bridge current could be quickly reversed by a double-pole tapping switch. This automatically compensates for a drifting bridge zero and doubles the bridge sensitivity. To further increase the sensitivity, a special galvanometer arrangement was used. A stationary mirror inside the galvanometer case was so placed that the beam of light from the movable galvanometer mirror was reflected back to the movable mirror before emerging to the scale. This arrangement doubles the deflection with less loss in light intensity than doubling the scale distance. With these arrangements, a sensitivity of 0.0001° C was attained.

For the purpose of automatic regulation of the envelope temperature, one resistance thermometer was inserted only to the region between the reference block envelope and condenser so that its temperature was quickly affected by the steam bath. This resistance thermometer was connected in a simple Wheatstone bridge and was used with a galvanometer, photelelectric cell, and amplifier to automatically maintain constant temperature of the steam bath.

7. AUXILIARY COOLING APPARATUS

Cold water was used for cooling the apparatus in the experiments below room temperature. About 30 liters of water circulating in a storage reservoir was cooled by an electric refrigerating unit and the temperature was controlled by a kerosene-filled thermostat. The cooled water from the reservoir was led by gravity through several different flow lines on the apparatus and emptied into a small centrifugal pump which returned it to the reservoir. The reservoir and flow lines were insulated with wool to avoid dew and excessive loss in refrigeration.

In all experiments starting near 0° C, the cooling water was maintained at a constant temperature by circulating over a layer of ice frozen to the refrigerator unit. In order to have the cooling water

temperature somewhat below 0° C to compensate for heating in the flow lines, enough ethyl alcohol was mixed with the water to lower the freezing point in the reservoir by the required amount. A special device was used for maintaining a covering of ice on the cooling unit. This device consisted of a straight tube with a small open end which rested against the unit. Thus tube was filled with water from the reservoir and the end sealed shut with ice as soon as ice began to form on the unit. Further freezing displaced the water in the tube and actuated the thermostat in the usual manner.

8. MEASURING INSTRUMENTS AND CALIBRATIONS

The water samples were weighed by the method of substitution, using a balance having a capacity of 2 kg. Below the balance pans there was a closed cabinet in which the water containers, tare containers, and counterpoises were suspended. The platinum-plated brass weights used were calibrated at this Bureau. Corrections were made for buoyancy of the air on the brass weights. Since the water sample is in a closed container, no correction for the air buoyancy on the sample is necessary. Correction for air buoyancy on the container was avoided by using counterpoises having approximately the same displacement as containers.

A Wolff-Diesselhorst potentiometer was used for measurements of current and potential drop in the calorimeter heater. A 0.1-ohm four-terminal resistor in series with the heater was used for the current determination and a 1,000 to 1 ratio volt box for the potential drop. Correction was made for the fraction of the main current shunted through the volt box, whose resistance was about 20,000 ohms. The potential drop in the calorimeter heater was measured by means of the two potential leads which join the current leads at points which had been chosen to account properly for the heat developed in the current leads between the calorimeter shell and envelope.

All electrical-measuring instruments were carefully calibrated several times during this series of experiments. The standard resistors and the volt boxes used were calibrated before, during, and after the series of measurements and showed no significant changes. The potentiometric measurements of power input were referred to a group of three cadmium standard cells. These cells were of the saturated type and were maintained at a constant temperature in a special temperature-controlled box described by Mueller and Stimson [7]. Frequent calibration of the standard cells proved their reliability to about a microvolt.

The Wolff-Diesselhorst potentiometer which was available for this work was not ideally adapted to these measurements. The calibration of the potentiometer showed a seasonal variation of nearly 1 part in 10,000 and a smaller daily variation. A scheme was devised using two permanent standard resistors to calibrate the potentiometer in place. By making this calibration two or three times a day, errors due to changes in the potentiometer were avoided.

The potentiometer was intended for use with standard cells having voltages between 1.01800 and 1.01930. The saturated standard cells at the temperature used in these experiments, however, gave about 1.01762 v. It was necessary, therefore, to set the potentiometer arbitrarily for some voltage in its range of adjustment and to correct for the true standard-cell voltage. In practice, the potentiometer

was set for a standard-cell electromotive force of 0.0005 v higher than that of the standard cells used, thereby giving a correction to each potentiometer reading of about 1 part in 2,036. This correction appears in the sample computation sheet as "correction for potentiometer ratio."

The description of the temperature-measuring instruments and their calibrations is given in the preceding section, "Thermometric installation."

Part 2. Heat Capacity of Water in the Range 0° to 100° C

I. INTRODUCTION

The heat capacity [2] of water has been the subject of various experimental determinations extending back to the time of Regnault. Some of them have been inspired by the usefulness of water as a calorimetric medium and definitive standard for determining heat capacities, while others have had for their objective the evaluation of the "mechanical equivalent of heat." The study of these past measurements for appraisal and correlation of results has been the subject of many reviews and reveals diligent effort to overcome inherent obstacles to accuracy in heat measurements by developing refinements of laboratory technique. During this development, the art of calorimetry has been far advanced by the evolution of standards and technique in electrical measurements of temperature and energy.

Notwithstanding all the advances in the laboratory arts, the appraisal of past experimental results has been unsatisfactory because so many uncertain factors have been involved regarding former units, standards, and calorimetric technique. Consequently, any interpretation of past results is subject to some arbitrary choice, and the various reviews have failed to bring the results into the accord to be expected from the accounts of the experimenters.

In 1921 the Cambridge, Mass. [8], conference on the properties of steam, as their first recommendation, made the proposal "the specific heat of water should be determined with the greatest possible accuracy up to the boiling point of water at atmospheric pressure for the more accurate determination of the mechanical equivalent of the mean heat unit."

Measurements made at the National Bureau of Standards and published in 1930 included data on the heat capacity of saturated water between 0° and 100° C., from which the specific heat at one atmosphere pressure could be derived. Since the experiments were not made especially for establishing accurate specific heats, the derived values were of only moderate precision. They have nevertheless been used in preference to earlier data as a basis for measurements of the enthalpy of superheated steam by several of the laboratories cooperating in the international steam research project. Recognizing that the accord of steam data was limited by the uncertainty in the values of the specific heat of water, the Third International Conference on Steam Tables [9], held in America in 1934, adopted a recommendation "that new measurements of the enthalpy or total heat of water between 0° and 100° C be undertaken by the National

[2] The expression "heat capacity" is used in this paper in the general sense of the energy required to produce a change of temperature, without necessarily restricting its application to unit mass, to unit temperature change, or to derivatives only.

Bureau of Standards to provide greater accuracy in these values for use in other calorimetric measurements." The present series of measurements was undertaken in response to this request and in extension of the program of steam research already completed.

In planning the work, it was the aim to provide for refinement of the technique of heat-balance accounting comparable with the accuracy of the temperature and power measurements, and if possible, to avoid an error of more than 1 part in 5,000 in the final results. To do this, it was necessary to design the new calorimetric equipment described in part 1 of this report.

II. METHOD AND APPARATUS

The method and apparatus have been described in detail in part 1 of this report, and therefore will be given only very brief mention here. The apparatus consisted essentially of a metal calorimeter shell containing a quantity of water, part liquid and part vapor. Immersed in the water are an electric heater and a circulating pump. Valves provide for filling and emptying the calorimeter. The calorimeter is well insulated from its surroundings, which are controlled to its temperature. Resistance thermometers and thermoelements are used in measuring temperatures.

In the measurement of heat capacity, the calorimeter with a sample of water was heated over a measured temperature range. By making some experiments with the calorimeter nearly full of liquid water, and others with it nearly empty, the tare heat capacity of the calorimeter was accounted for and there was obtained the change of a quantity called alpha, α, which is a property of the water alone. This quantity alpha differs from the enthalpy, or heat content, H, of saturated liquid water by another quantity beta, β. In other words,

$$\alpha = H - \beta$$

The quantity beta, β, had been measured calorimetrically in previous experiments at higher temperatures. However, between 0° and 100° C, it is so small that its value can be calculated from other data with greater accuracy than can be obtained by calorimetric measurements.

In addition to the enthalpy, H, of saturated liquid, values of specific heat, etc., may be derived.

III. EXPERIMENTAL PROCEDURE

In the heat-capacity measurements it was necessary to measure the amount of water subjected to the process, the amount of energy exchanged, and the change in state produced. It was the aim to account accurately for all three of these main factors. The following description of the experimental procedure indicates how these essential accountings were made.

1. ACCOUNTING FOR MASS OF WATER

The mass of water subjected to a change of state enters as a direct factor in the reduction of the data. The results, therefore, would be no more reliable than the determinations of the masses. Special care was therefore taken that the weighings were accurate and free from systematic errors. An account was kept of the amount in the calorim-

eter at any time and a check made by completely exhausting and weighing each charge before refilling with a new one.

The water used in these experiments was purified by preliminary distillation and then redistilled in a specially designed still under a pressure of about 0.1 atmosphere for the purpose of removing dissolved gases. These gases were removed by continuously withdrawing a part of the mixture of gas and water vapor from the condenser of the still. This kept the partial pressure of the gas at the condensing surface less than 0.001 atmosphere. The fraction of gas dissolving in the condensing water at this low pressure was too small to have any significant effect on any of the measurements.

The purified sample of water was then transferred from the still to an evacuated container, which was then weighed. When filling the calorimeter, this container was connected to the evacuated calorimeter, as shown in figure 3, and the connecting line evacuated. The water was transferred by gravity from the container to the calorimeter, leaving only a few grams in the container and line. The water in the line was collected and weighed by pumping through a detachable liquid-air trap in the vacuum line. The container with the water remaining in it was then reweighed. From the weights of the container before and after filling the calorimeter, and the weight of the water from the line, the amount of the water in the calorimeter was obtained by differences. When emptying the calorimeter, a similar procedure was followed, except that the water container was placed below the calorimeter, so that the water would flow from the calorimeter down to the container. The water remaining in the line and calorimeter was accounted for by condensing in liquid air and weighing as before.

The same charge of water was usually left in the calorimeter for several days' experiments. Comparison of the amount put in with the amount taken out was a check on the accuracy of accounting for the mass. Such a sum check was carefully kept in this work, and when the accounts did not agree, the results were discarded. Usually the check was to about 0.020 g, which amounts to about 1 part in 50,000 in a 1-kg water sample.

2. ACCOUNTING FOR ENERGY

Measured energy was supplied electrically to the calorimeter and contents by means of the calorimeter heating coil installed within the calorimeter shell and immersed in the water sample. Power was supplied by a separate storage battery of large current capacity. Potentiometer readings of current and potential drop across the calorimeter heater were made periodically for obtaining the energy added electrically, as described later. Reduction of these readings took account of the timing of the readings and of the slight gradual change in power which sometimes occurred.

In order to avoid too rapid an initial change when the current was switched to the calorimeter heater at the start of an experiment, a substitute resistor was used to steady the battery output. Between heating periods, the battery current was adjusted to a selected value to make the final temperature of the calorimeter come close to the desired even temperature after the power had been on an integral number of minutes. It was usually possible to adjust the current,

so that the final temperature would be within 0.01° C of the desired temperature.

The resistance of the calorimeter heater increased, during the first few seconds after the power was switched on, until the resistor temperature had reached a steady value. Since this change was practically completed before the first current reading was made (½ min after the start), the correction for it was determined by separate experiments. The correction for the current change was found by leaving the galvanometer connected when the currect was shifted to the calorimeter and observing the deflections periodically for 15 sec. The integral of the galvanometer deflections over this time was used to compute the starting correction to the current. The starting correction for the potential drop, which is of the opposite sign, was obtained in a similar manner. These corrections were then combined to get the energy correction. This amounted to only 1 part in 10,000 of the whole energy input, even in the extreme case.

The shift in current from the substitute resistor to the calorimeter heater, was made automatically by means of double-pole double-throw switch, which was actuated by a tensed spring and released by the electric seconds-signals furnished by the standard clock. Since the heating periods were integral numbers of minutes, no significant errors have been attributed to the mechanism for transmitting the electric signals from the clock. Some experiments made to determine the time error due to the switch showed it to be 0.002 sec. or less and therefore insignificant.

The auxiliary electrical-measuring apparatus used in the measurement of the power and its calibration have been described in part I. The routine of current and potential-drop observations for evaluating the power input are described later in the description of heat-capacity measurements.

The small amount of energy transmitted to the calorimeter by the pump and appearing as heat added was included in the accounting for total energy added in any experiment. The pump speed was kept constant at approximately 70 rpm, by a geared drive from a synchronous motor. Determinations of the pump power thus dissipated as heat were a part of the regular routine of the entire experimental program. These determinations were made calorimetrically by observing the rise in temperature produced in the calorimeter by running the pump alone with no electric-power input, keeping control and account of heat leak just as in a heat-capacity measurement. These pump-power experiments usually lasted for half an hour and the energy per minute was derived for each.

About 70 pump-power determination were made during the series of heat-capacity experiments. Pump-power determinations were made with both large and small masses of water in the calorimeter and, at one time or another, at most of the even temperatures where stops were made in the experiments. These determinations gave values of pump power about 0.2 to 0.3 j/min. After a study of the resulting values of pump power, simple formations were derived for use in calculating pump energies in the heat-capacity experiments.

The accidental variation of the observed pump power from the general mean was larger than could be accounted for by the uncertainty of the temperature measurement, but this was usually not more than would correspond to about 1 part in 20,000 in the value of alpha.

The characteristics of the pump, i. e., speed, power input, and corresponding heat-distributing effect, had been investigated by preliminary measurements before installing the pump in the calorimeter shell and served as a guide in choice of speed for the most advantageous operation in the final measurements.

The control and evaluation of heat leak is a vital part of any calorimetry when high precision is sought. The means provided for this purpose have been described in part 1. In operation, there were usually slight deviations from the ideal control which would nullify heat leak. The small corrections for this remaining heat leak were evaluated with the aid of the differential thermoelements, which indicated temperature differences between the calorimeter and its envelope by the number of microvolts. These differences were observed every minute and added algebraically to give sums in microvolt-minutes, called "heat-leak factors." These factors, when multiplied by "heat-leak coefficients," give the heat-leak corrections for the individual experiments. As previously stated in another way, the calorimeter was designed to make the coefficient small by construction and by evacuation of the insulating space, and means were provided to make the factor small by manipulation of the envelope temperature.

The total heat leak as determined experimentally consists of several parts, designated as "envelope," "upper-tube," and "lower-tube" heat leaks. The envelope heat leak is the chief part and results mainly from radiation between the surface of the calorimeter and of the envelope. The two tube heat leaks account for the heat transfer by metallic conduction along the tubes between the calorimeter and envelope. These tube heat leaks were nearly proportional to the envelope heat leak but not always exactly so for all experimental conditions, and therefore they were corrected for separately. Their coefficients were computed with sufficient accuracy from the knowledge of their dimensions and the thermal conductivity of their material.

The envelope heat-leak coefficient (in joules per microvolt-minute) was determined experimentally during the early part of the program and were checked occasionally later. This was done by exaggerating the temperature difference between the envelope and the calorimeter for a suitable time, observing this temperature difference and the two tube-temperature gradients every minute by means of the thermoelements, and summing these thermoelement indications (in microvolt-minutes) for the whole period to give the heat-leak factor. The total energy change in the calorimeter was computed from the measurements of the calorimeter temperature before and after this exaggerated heat leak. This energy, when corrected for the pump energy and the upper- and lower-tube heat leaks, was divided by the heat-leak factor, to give the envelope heat-leak coefficient, in joules per microvolt-minute, at the mean temperature of the experiment. This coefficient included, beside the radiation, any conduction (except by the two tubes) which was proportional to the temperature difference between the shells. This accounted for conduction through the heater and thermoelement wires. The gaseous conduction between these shells was probably negligible with the evacuation (less than 0.000,001-atmosphere pressure) maintained during all the experiments.

The factors of the three heat leaks were determined from observations made every minute during the experiments and were summed

algebraically for the whole periods. The experimental manipulation was usually such as to make the envelope heat-leak factor very small. During the heat-capacity experiments, the entire heat-leak correction would seldom affect the individual results by as much as 1 part in 50,000. It might be thought that corrections as small as these could have been disregarded, but had they not been regularly observed there would be no assurance that they were always insignificant.

The lower tube was always full of liquid, and precautions were taken to keep this tube always cool enough to prevent boiling, which might have caused transfer of heat to the calorimeter.

In addition to the various heat leaks mentioned, there is the possibility of a residual heat leak which could have been overlooked in the accounting for energy. This residual heat leak would be one which still occurred when everything else was eliminated and could be observed during periods when the pump was stopped and all other heat-leak factors kept as near zero as possible. A few such experiments were made but gave little more than a detectable coefficient. These experiments were discontinued, because whatever this residual heat leak was, it was included always in determinations of the pump power and therefore not neglected.

In the heat-capacity experiments, the usual procedure was to start observing the calorimeter temperature at 3 min after the end of the heating period. Investigation showed that thermal equilibrium was not complete in that time and that a small correction should be made if that temperature were used. This correction was found to be a function of the amount of water in the calorimeter and the temperature of the experiment. Although it was very small, it was applied to all heat-capacity experiments.

3. ACCOUNTING FOR CHANGE IN STATE

The temperature of the calorimeter and contents was measured by a platinum resistance thermometer used in conjunction with thermoelements, as previously described. The temperature change of the calorimeter and contained water sample was thus accurately observed in all experiments. All observed temperatures are expressed on the International Temperature Scale.

For determining either the initial or final temperature, each temperature reading consisted in simultaneous observations of resistance thermometer and thermoelements. The eight thermoelements on the calorimeter were connected in series to indicate the mean temperature of the calorimeter with respect to the reference block. Four successive temperature readings were made at half-minute intervals. This method of making several successive temperature readings is desirable for several reasons. The four-lead potential-terminal resistance thermometer requires at least two observations to eliminate the lead resistance from the measurement. Increasing the number of readings decreases the accidental error of observation. A regular schedule of readings takes account of slight drift in temperature.

A change in the proportion of liquid and vapor in the calorimeter occurs in the experiments. This change is analyzed in the theory of the method and is accounted for by use of the supplementary quantity, which is designated as β.

Special details of the experimental procedure that apply to the carrying out of the calorimetric measurements will next be described.

4. DESCRIPTION OF HEAT-CAPACITY MEASUREMENTS

It will be recalled that these experiments yield values of the change with temperature of the quantity α. Combined algebraically with corresponding changes of the quantity β, obtained from calculations, the data suffice to determine the change in enthalpy, H, of the saturated liquid.

The procedure in these heat-capacity experiments consisted essentially in heating a sample of water, part liquid and part vapor, over an accurately measured temperature range and in accounting for the energy added in the process. Two such heat-capacity determinations, a gross and a tare, are required for an evaluation of the change in α. These two determinations over the same temperature interval are made with different amounts of water, always maintaining the saturation condition. One determination, made with a large charge, yields a gross value of energy added. The other, made with a small charge, yields a tare value. The difference, or net value, of energy added, divided by the net mass, gives the value of the change in α for that temperature interval. This method of differences avoids the necessity of determining the heat capacity of the empty calorimeter.

In an experiment starting, for example at 0° C, the calorimeter is first cooled by the following procedure. The cold water from the cooling tank, where the temperature is a few tenths of a degree below 0° C, flows through the condenser (*W1* in fig. 3) located at the top of the main steam jacket, the condenser, *W2*, located at the top of the reference block steam jacket, the guard cooling coil, *W3*, and the stuffing-box cooling cell, *W4*. The space between the envelope and calorimeter is filled with helium to increase heat transfer between the two. Heat from the calorimeter and contents is transferred to the colder surroundings until the temperature of the calorimeter and contents is about 0° C. This process took many hours when the calorimeter contained a large charge and was usually done overnight. In a few of the experiments starting near zero the temperature of the calorimeter and contents was reduced to a few hundredths of a degree below zero. At no time was there any evidence of freezing in the calorimeter.

The envelope and the reference block are then brought to the temperature of the calorimeter. The helium is then pumped out of the envelope space to reduce heat transfer. The circulating pump is started at the desired speed, and the apparatus is ready for the beginning of an experiment.

The equilibrium temperature of the calorimeter and its contents is observed as described in section 3. The storage battery is connected to the calorimeter heater by the switch actuated by the time signals. At about the same time, the power is supplied to the envelope heater and reference-block heater. The currents in these heaters are adjusted so that the temperatures of the envelope and reference block stay very close to the temperature of the calorimeter. The differential thermoelement indications for determining the heat leak are observed almost continuously and recorded once each minute. One or more complete surveys with all thermoelement combinations are usually recorded in each individual experiment. The current and potential drop in the calorimeter heater are observed on alternate minutes starting with the first half-minute of the interval. The calorimeter heating

is continued for an integral number of minutes and stopped when the desired temperature interval has been completed.

The rate of heating was chosen as 0.5° C/min, and the calorimeter heater current was adjusted before the beginning of each experiment, so that after the integral number of minutes, the calorimeter temperature ended very close to the desired even temperature. The envelope and reference-block heater currents were adjustable to keep the temperatures of the envelope and reference block very near that of the calorimeter at all times. After several minutes, to allow the calorimeter and contents to come to temperature equlibrium, the final temperature was observed. This completed the heat-capacity experiment.

Two groups of such experiments were made, one with large charges of water in the calorimeter and the other with small charges. The experiments with small charges may be regarded as determinations of the tare-heat capacity of the calorimeter. Choice of the extent of the temperature intervals was governed by the rate of change of heat capacity with temperature. It was found that 10° intervals were suitable to determine the trend over most of the temperature range. Toward 0° C, where the change was increasingly rapid, the shorter intervals of 5°, 2.5°, and finally 1° C, gave more convincing evidence about this rate of change, even at the cost of some loss in the percentage of accuracy of the intervals.

During the heat-capacity experiments, the upper tube was closed at both its upper and lower ends by metal disks. In this way, possible error from condensation of water in the upper tube was avoided.

IV. RESULTS OF HEAT-CAPACITY EXPERIMENTS

The observations made during the experiments were recorded on separate laboratory-data sheets as soon as they were made. The computations from these sheets were often begun before all of the day's data sheets had been completed, and it was the rule to have preliminary results of the data for one day before the experiments of the next day were under way. This made it possible to arrange the day's observations with the full knowledge of what was most needed and what special precautions, if any, needed to be taken in observing. As more data were collected, it was possible to get and use more complete knowledge of contributory results, such as pump power, heat-leak coefficients, etc., that enter into the final reductions. Lastly, corrections were made for all known factors. The energies thus determined for the actual temperature intervals were then interpolated to even temperature intervals. These were reduced to determinations of the change of α over separate temperature intervals. These data were then formulated for use in the computation of tables and for computations involving the heat capacity of water.

In table 1, a typical data sheet is shown for a "large-mass" experiment made with 1,093.647 g of water in the calorimeter. The observations recorded under "Power" consist of the potentiometer readings of potential drop and current in the calorimeter heater after applying the decimal factors for standard resistor and volt box to reduce the readings to volts and amperes. Under "Thermometer" are given both "normal" (N) and "reverse" (R) bridge readings of the resistance of the thermometer in the reference block. The remaining observations are thermoelement readings, in microvolts. The column "Calorimeter minus reference block" shows the thermoelement readings of the eight

thermoelements ($JT+JB$) used in the measurement of the average temperature of the calorimeter. Under "Envelope minus calorimeter" are recorded the readings of the eight thermoelements on the envelope ($JU+JL$) opposed to the eight on the calorimeter ($JT+JB$). The column "Lower tube" shows the indications of the thermoelements ($J9-J8$), while the column "Upper tube" shows ($J7-J5$). In the last column, a survey of thermoelement indications is shown, starting just after the routine observations at 11:57. At least one such survey, taking less than a minute, was made in each experiment.

TABLE 1.—*Sample data sheet*

[Temperature interval 25° to 30° C ..... October 27, 1937]

Time	Power		Thermometer, Bridge readings	Thermoelement readings				
	Potential drop	Current		Calorimeter minus reference block	Envelope minus calorimeter	Lower tube	Upper tube	Survey of other thermoelements
	v	*amp*	*Ohms*	*μv*	*μv*	*μv*	*μv*	*μv*
11:53			30.41524 N	−0.4	1	−1	0	
53.5			30.41517 R	−.5				
54			30.41516 R	−.5	2			
54.5			30.41524 N	−.6				
55	On				1	−1	0	
55.5		0.60268						
					2	−3	5	
56.5	65.965							
				0	0	−3	5	
57.5		.60269						JU 1
					0	−3	5	JL 1
58.5	65.965							JT 0
					−1			JB −1
59.5		.60274						J1 0
					−1	−4	5	J5 −12
12:00.5	65.964							J8 −2
					0			J10 −3
01.5		.60278						
					0	−3	5	
02.5	65.963							
					−1			
03.5		.60283						
					−1	−3	5	
04.5	65.963							
05	Off				−1			
06					−2			
07					0			
08			30.96171 N	−0.3	2			
08.5			30.96162 R	−.3				
09			30.96165 R	−.4	0	−1	0	
09.5			30.96171 N	−.5				

Table 2 shows a computation sheet, using the data given in table 1. The first step is the calculation of the temperature of the calorimeter. The average of the first four bridge readings is taken as the resistance of the thermometer at the mean time. Using the thermometer and bridge calibrations, the temperature of the reference block corresponding to this resistance value is obtained. Likewise, the average of the first four readings of the thermoelements ($JT+JB$) is found and from this and the calibrations, the difference in temperature called "temp. cal. minus temp. ref. block" is obtained at the same mean time. Combination of these temperature measurements gives the initial temperature of the calorimeter at that time, considered as the beginning of the experiment. The same method is used in the computation of the final temperature.

TABLE 2.—*Sample computation sheet, using data shown in table 1*

[Temperature interval 25° to 30° C ..... October 27, 1937]

Steps in computations	Temperature	
	Initial	Final
Average of bridge readings ..... (ohms)	30.41520	30.96167
Temperature of reference block ..... (°C)	25.0034	30.003
Average thermoelement reading ..... (μv)	−0.50	−0.38
Temp. cal. minus temp. ref. block ..... (°C)	− 0.0010	−0.000
Temperature of calorimeter ..... (°C)	25.0024	30.002

	Energy	
	Potential drop	Current
	v	*amp*
Average of potentiometer readings	65.9640	0.60274
Correction for timing of readings	0.0001	.00005
Potentiometer calibration correction	.0090	.00090
Correction for potentiometer ratio	−.0324	−.00256
Volt-box current		−.00328
Correction for volt-box factor	.0011	
Correction for standard resistance factor		−.00086
	65.9418	0.59163
	int. j	
Electric energy for 600 sec	23,705.9	
Pump energy for 15 min	3.7	
Envelope heat leak (for $-2\ \mu v$ min)	0.0	
Lower tube heat leak (for $-36\ \mu v$ min)	−.1	
Upper tube heat leak (for $50\ \mu v$ min)	0.3	
Starting correction	2.3	
Equilibrium correction	−0.2	
Energy added to calorimeter and contents	23,711.9	
Energy to correct initial temp. to 25° C	11.4	
Energy to correct final temp. to 30° C	−13.3	
Energy for even temp. interval, 25° to 30° C	23,710.0	

The next step is the computation of the electric-energy input to the calorimeter during the heating period, 11:55 to 12:05. The potential drop across the calorimeter heater is calculated from the average of the five potentiometer readings of potential drop. Since these potentiometer readings are not distributed symmetrically about the middle of the heating period, a small correction is made to account for the drift during the experiment. This is recorded as "correction for timing of readings." The "potentiometer calibration correction" is computed, taking into account the calibrations made during the day of the experiment. The "correction for potentiometer ratio" has been explained in part 1 of this report under "measuring instruments and calibrations." The correction for the volt-box calibration factor is also recorded. Applying all of these corrections to the average of the potentiometer readings, the average calorimeter potential drop, expressed in international volts, is computed.

Likewise, the average calorimeter heater current (international amperes) is computed. In this case, corrections must be made for the current through the volt box and for the standard 0.1-ohm calibration factor. By multiplying together the current, the potential drop, and the time of electric heating (600 sec), the total electric energy (international joules) is computed.

The next step is the computation of the total energy added to the calorimeter and contents during the experiment. This is obtained by adding to the total electric energy the following small energy corrections. The pump energy is calculated from the value of power formulated from pump-power experiments. This pump power was multiplied by the time of the experiment (15 min) to give the pump energy. The three heat leaks (envelope, upper tube, and lower tube) were computed by summing the thermoelement readings from table 1 to give heat-leak factors in microvolt-minutes. These factors were multiplied by their respective heat-leak coefficients to give the heat-leak corrections. The "starting correction" and "equilibrium correction," which have been described in the previous section, were calculated from the results of the special experiments. The sum of the electric energy and all the energy corrections gives the entire energy added to heat the calorimeter and its contents from the initial temperature, 25.0024° C, to the final temperature, 30.0028° C.

In the reduction of the results, it was convenient to use the even temperature interval 25° to 30° C. Therefore, corrections were made for the small deviations of the measured temperatures from the intended even temperatures. Only approximate values of the heat capacity of the calorimeter and contents were necessary to make these corrections. The resulting energy is recorded as "energy for even temperature interval," and will be referred to as ΔQ.

The sample computation just described is one of the 256 assembled in table 3. This table contains the substance of the principal data and preliminary reductions of the heat-capacity experiments made with a large mass of water in the calorimeter. Table 4 contains a similar assembly of the principal data of the 137 experiments made with a small mass of water. These two tables comprise an abstract of the record of all the experimental data which were accepted as trustworthy. Only those experiments in which the technique was faulty or the record incomplete were excluded. Further reductions of these data are included in these tables, as next described.

Each experiment for the temperature interval Δt gives a value of ΔQ which, according to the theory [1], should satisfy the equation

$$\frac{\Delta Q}{\Delta t}=\frac{\Delta Z}{\Delta t}+\frac{M\Delta\alpha}{\Delta t},$$

where M is the mass of water in the calorimeter, $\Delta Z/\Delta t$ is a property of the calorimeter independent of the amount of water in it, and $\Delta\alpha/\Delta t$ is a specific property of the water. By taking all the equations for one temperature interval for both the large- and small-mass experiments, it is possible to solve for the $\Delta\alpha/\Delta t$ and $\Delta Z/\Delta t$ for that interval by the method of least squares, as was done in previous publications. Actually, however, since approximate values of $\Delta\alpha/\Delta t$ were available from previous researches, it was found expedient to solve for preliminary values of $\Delta Z/\Delta t$ as the experimental work progressed, using these tentative values of $\Delta\alpha/\Delta t$ together with the data from experiments with small mass. These values of $\Delta Z/\Delta t$ were smoothed by formulating dZ/dt and were then used with the large-mass data to compute corresponding values of $\Delta\alpha/\Delta t$. Successive substitutions of these tentative values of $\Delta Z/\Delta t$ and $\Delta\alpha/\Delta t$ gave rapid approach to the limiting mean values, since the ratio of the large to the small masses was usually about 8.6. This method of reduction facilitated

the preliminary survey of results as the experimental data accumulated and served as a guide in the choice of temperature intervals best suited to determine the trend of the heat-capacity curve.

As finally reduced and recorded in table 4, the result of each experiment with small mass constitutes a separate determination of $\Delta Z/\Delta t$, and the entire series of these results is a calibration of the calorimeter. Similarly, the result of each experiment with large mass, as reduced by use of the calibration results and recorded in table 3, constitutes a separate determination of $\Delta\alpha/\Delta t$, and the entire series is a determination of the heat capacity of water in the range 0° to 100° C.

A comparison of the individual results with the average values indicates the degree of consistency of the measurements, and comparison of the averages with the formulated values indicates the degree of consistency of the trend with temperature. The manner of formulation of these results will next be described.

Since all experiments are necessarily made over finite temperature intervals, the results, in terms of increments $\Delta\alpha/\Delta t$ and $\Delta Z/\Delta t$, differ slightly from the corresponding derivatives, $d\alpha/dt$ and dZ/dt. These differences were computed by use of preliminary approximate equations and were used to get the corresponding values of $d\alpha/dt$ and dZ/dt[6] at the mid temperatures to be fitted by formulas.

The empirical formula chosen for dZ/dt has the following form:

$$dZ/dt = A + Bt + C(t+60)^{5.14}.$$

The final coefficients determined from the average values of $\Delta Z/\Delta t$ listed in table 4 are $A=168.69$, $B=0.089$, and $C=68.85214\times10^{-10}$, where t is in degrees centigrade and dZ/dt is in international joules per degree centigrade. Values of $\Delta Z/\Delta t$ calculated from this formula are given in table 4 as formulated values of $\Delta Z/\Delta t$. It appears that a further adjustment of the dZ/dt formulation by another approximation would have changed the final value of $d\alpha/dt$ by about 1 part in 80,000 at 0° C and by successively smaller amounts up to 100° C. This change was considered as sufficiently insignificant to be neglected.

The formulation for $d\alpha/dt$ was based on the values of $\Delta\alpha/\Delta t$ given in table 3. The average values of $\Delta\alpha/\Delta t$ were computed for each of the 20 temperature intervals and then corrected for deviations from the derivatives to get corresponding mean values of $d\alpha/dt$. It is obvious that some of these experimental means should have more weight than others. For example, the 19 experiments over the 10° interval from 40° to 50° C should have more weight than the 4 experiments over the 1° interval from 0° to 1° C. The means were therefore weighted approximately proportionally to the number of experiments times the number of degrees in the interval. A least-squares solution was then made for the constants in the following empirical equation:

$$d\alpha/dt = A + Bt + C(10)^{-0.036t}.$$

The constants were found to be $A=4.1699$, $B=0.000\,015\,27$, and $C=0.0467$, where t is in degrees centigrade, and $d\alpha/dt$ is in international joules per gram-degree centigrade. Using this equation, the values of $\Delta\alpha/\Delta t$ for each of the intervals have been computed and are recorded in table 3 for each interval. The deviations from these formulated values are tabulated in the last column of table 3.

It may be seen from table 3 that in the later experiments there is a trend to lower values of $\Delta\alpha/\Delta t$. The experiments above 5° C made after October 28, 1937, show values of $\Delta\alpha/\Delta t$ which average about 1 part in 10,000 less than those before that date. No explanation is offered for this change, and the fact is taken merely as evidence of the limitation of accuracy due to unknown systematic causes.

Since the specific heat at ordinary atmospheric pressure is the property of water most commonly utilized for calorimetric purposes, this property was determined by further reduction of the experimental average values of $\Delta\alpha/\Delta t$ given in table 3. This computation will next be described.

The reduction may be considered in three steps, which are indicated in table 5, starting with the average of the measured values of $\Delta\alpha/\Delta t$. At saturation pressure, the mean enthalpy change, $\Delta H/\Delta t$, exceeds $\Delta\alpha/\Delta t$ by the quantity $\Delta\beta/\Delta t$, as shown in the theory. The values of this reduction term, as given in column 3, were calculated by the relation $\beta = TudP/dT$, as explained in part 1 of this report. Values of the specific volume, u, were obtained from the density data of Chappuis [10] up to 50° C and of Thiesen [11] up to 100° C, and the compressibility data of Smith and Keyes [12]. Values of dP/dT were obtained from an unpublished formulation of the vapor-pressure data of the Reichsanstalt as reformulated by Harold T. Gerry and used for the saturation pressure table by the International Steam Conference of 1934 [9, 36].

Next, values of the term for reduction to mean enthalpy change at 1-atmosphere pressure, $(\Delta H/\Delta t)_{p=1} - (\Delta H/\Delta t)_{sat.}$, as given in column 4, were calculated by the relation

$$\left(\frac{dH}{dP}\right)_T = V - T\left(\frac{dV}{dT}\right)_p,$$

using the same data as above. There is still the difference between the mean value of the change of enthalpy per degree at 1 atmosphere and the derivative, $C_{p=1}$, the desired specific-heat value at the mid-temperature of the interval. This reduction term, $C_{p=1} - (\Delta H/\Delta t)_{p=1}$, given in column 5, was computed by using a preliminary approximate equation for C_p.

The 20 experimental values of C_p in column 6, which were obtained by applying the three reduction terms just described, were then formulated, using the same weighting factors previously used in the formulation of $d\alpha/dt$. After tests of types of functions to represent the experimental data, the empirical equation finally chosen was

$$C_p = A + B(t+100)^{5.26} + C(10)^{-0.036t}.$$

The coefficients were determined by least squares to be $A = 4.169\,036$, $B = 0.000\,3639(10)^{-10}$, and $C = 0.0467$, when t is expressed in degrees centigrade, and C_p in international joules per gram-degree centigrade at 1-atmosphere pressure. Both the formulated and the experimental values of C_p are given in table 5, together with the deviations. The midtemperatures of the temperature intervals are given also.

Figure 4 shows graphically the comparison of the experimental values with the formulated values of C_p. In this figure the areas of the circles representing the observed means are made proportional to the weights assigned in the formulation. In other words, the larger

circles indicate that more experiments or larger temperature intervals are represented. The degree of accord of the formulation with the experimental results shows that this fairly simple empirical equation is adequate to represent the results over the entire 100° C range. However, this agreement must not be taken as an estimate of the accuracy of the results, since it takes no account of unknown systematic errors, which may well be larger than the accidental errors.

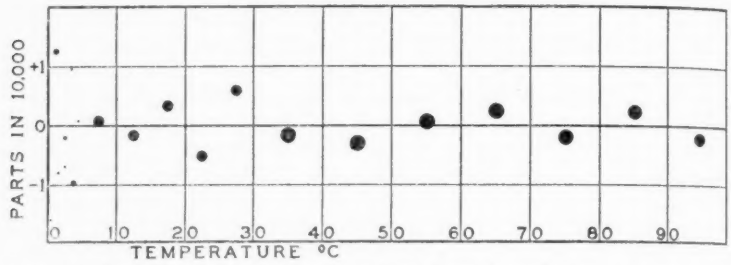

FIGURE 4.—*Deviations of mean measured C_p from formulation. Areas of circles are proportional to the weights assigned to the mean values.*

Figure 5 shows a comparison of the heat capacities. It should be noted from the figure that the scale of the heat capacities is very much exaggerated and that the extreme range of the values of C_{p1} between 0° and 100° C is only about 1 percent. The $d\alpha/dt$ line gives essentially the measured values of heat capacity. The departure of the $(dH/dt)_{sat}$ line from the $d\alpha/dt$ line represents the magnitude of the $d\beta/dt$ reduction. The difference between the C_p line and the

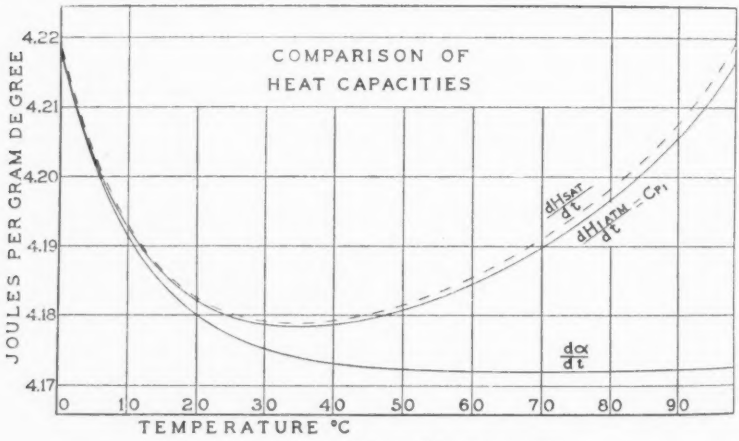

FIGURE 5.—*Comparison of heat capacities.*

$(dH/dt)_{sat}$ line shows the magnitude of the reduction to 1-atmosphere pressure. The experimental values have not been plotted on this figure, because only one or two values would fall outside the width of the line in spite of the exaggerated scale.

Water is often used as a calorimetric medium and also as a standard of heat capacity, as, for example, in a condensing calorimeter for measuring the enthalpy of superheated steam or for measuring

specific heats by the method of mixtures. For such purposes, it is useful to know the integral of the specific heat (C_p) function, since these calorimetric measurements must necessarily apply to finite temperature intervals. A table of values of the integral, giving the heat content, or enthalpy, from 0 to each temperature at intervals of 1° from 0° to 100° C has been prepared for this use. This table has been compiled in terms of absolute joules per gram and international steam-table calories per gram instead of any of the numerous heat units which have been used in the past, and defined variously in terms of the heat capacity of water.

Since the absolute practical electrical units are expected to replace the present international units on January 1, 1940, it seems desirable to use the absolute joule rather than the international joule which has been used in the measurements, but which is likely so soon to be obsolete. Also since the international steam-table calorie (IT Cal), defined as 1/860 int. whr, has now become the basis of heat units used in steam tables, values are included in this unit.

The conversion factor from international joules to absolute joules, being based on measurement, can not be exactly known, but the uncertainty has been greatly reduced by the more recent measurements of the absolute ohm and absolute ampere in terms of the electrical standards maintained in National laboratories. Since a final official figure for this factor has not yet been announced, the value 1 int. j=1.00019 abs. j used here was an estimate of the probable value of the absolute joule in international joules as derived from electrical standards maintained in this laboratory and was based on recent measurements, partly unpublished. It is believed that this value expresses the equivalent of the units actually used within 1 or 2 units in the last place.

The equation for C_p in international joules per gram-degree centigrade has been converted to absolute joules per gram-degree by multiplying the coefficients by the factor 1.00019, giving the new equation

$$C_p=4.169828+0.000364(t+100)^{5.26}\times10^{-10}+0.046709(10)^{-0.036t},$$

where t is in degrees centigrade and C_p is in absolute joules per gram-degree centigrade at 1-atmosphere pressure. By integration of $C_p dt$, the equation for enthalpy, H_p, at 1-atmosphere pressure in absolute joules per gram is obtained. Taking the value of $H_{sat.}$ as 0 at 0° C, the equation is

$$H_p=0.102559+4.16928t+[5.8142(t+100)^{6.26}\times10^{-15}-0.563485(10)^{-0.036t}]^{t}_{0},$$

where t is in degrees centigrade, and H_p in absolute joules per gram at 1-atmosphere pressure.

Values of both C_p and H_p are given in table 6. The values of H_p, in IT Cal, have been computed from the values in absolute joules per gram by use of the conversion factor 1 abs. j=0.238846 IT Cal.

This gives values of H_p which are larger by 1 part in 100,000 than correspond to the present definition of the IT Cal but are in agreement with a redefinition of the IT Cal as 0.001163 abs. whr, which has been suggested for adoption when the change in electrical units takes place. This small discrepancy is less than the amount which is important in steam tables, and likewise less than the uncertainty of the present measurements.

The enthalpy of saturated liquid water is one of the important items in the compilation of steam tables. Values of this property were computed by use of the formula for $d\alpha/dt$ and values of β.

The formula for $d\alpha/dt$ in international joules per gram-degree centigrade is

$$d\alpha/dt = 4.1699 + 15.27\ t \times 10^{-6} + 0.0467(10)^{-0.036t}.$$

By integration, the following equation for the increment of α is obtained:

$$\alpha^t_0 = [4.1699t + 7.635t^2 \times 10^{-6} - 0.56376 \times 10^{-0.036t}]^t_0.$$

Values of α^t_0 computed by this equation, at every 5° point from 0° to 100° C, are given in table 7. Values of β, computed as previously described, are also given. Values of enthalpy are found by adding the increment of β to α^t_0, and are given in the table in international joules per gram and also converted to absolute joules per gram and to International Steam Table Calories per gram, using the conversion factors stated above.

TABLE 3.—*Principal data from large-mass heat-capacity experiments*

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	*°C*	*°C*	*Int. j*	*Int. j*	*Int. j*	*Int. j/g-°C*	*Int. j/g-°C*
12-7-37	1093.989	0.0104	0.9974	0.0	1.7	4,778.4	4.21286	−0.00187
12-9-37	603.781	.0565	.9522	.0	6.1	2,714.9	4.21563	.00090
12-10-37	603.781	.3232	1.0068	.1	15.6	2,713.9	4.21398	−.00075
12-14-37	603.781	.0324	.9938	.0	2.9	2,713.9	4.21398	−.00075
Average							4.21411	
Even temperature interval 0.0° to 1.0° C. $\Delta Z/\Delta t$=169.577 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.21473 int. j/g-°C								
9-23-37	1091.161	0.1772	2.4587	0.6	2.7	11,918.6	4.21363	0.00153
10-6-37	1092.517	.4886	2.4624	−.1	2.4	11,932.5	4.21349	.00139
10-8-37	1092.517	.2433	2.4981	−.4	2.7	11,931.7	4.21320	.00110
10-14-37	1092.517	.1884	2.4990	−.2	2.4	11,932.1	4.21334	.00124
10-21-37	1093.647	−.0385	2.5184	−.1	2.4	11,939.6	4.21173	−.00037
10-26-37	1093.647	−.0376	2.4947	−.1	2.4	11,941.4	4.21239	.00029
10-27-37	1093.647	.0120	2.4972	.2	2.4	11,941.1	4.21228	.00018
10-28-37	1093.647	.0070	2.4992	.1	2.4	11,941.1	4.21228	.00018
11-16-37	1096.489	−.0174	2.4588	.0	2.4	11,970.4	4.21205	−.00005
11-18-37	1096.489	−.0037	2.4867	−.1	2.4	11,971.1	4.21231	.00021
12-2-37	1093.989	−.0586	2.5191	.4	2.9	11,945.7	4.21265	.00055
Average							4.21267	
Even temperature interval 0.0° to 2.5° C. $\Delta Z/\Delta t$=169.688 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.21210 int. j/g-°C								
9-14-37	1091.161	0.1830	4.9763	1.3	5.6	23,809.2	4.20833	0.00036
9-21-37	1091.161	.1920	5.1873	.5	4.1	23,806.8	4.20789	−.00028
Average							4.20811	
Even temperature interval 0.0° to 5.0° C. $\Delta Z/\Delta t$=169.879 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.20817 int. j/g-°C								
12-7-37	1093.989	1.0078	2.0054	−0.1	1.7	4,776.7	4.21118	0.00000
12-9-37	603.781	.9518	1.9649	.0	6.1	2,712.3	4.21109	−.00009
12-10-37	603.781	1.0041	2.0051	.0	15.6	2,712.2	4.21093	−.00025
12-14-37	603.781	.9964	1.9944	.0	2.9	2,711.8	4.21027	.00009
Average							4.21087	
Even temperature interval of 1.0° to 2.0° C. $\Delta Z/\Delta t$=169.725 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.21118 int. j/g-°C								

TABLE 3.—*Principal data from large-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/g-°C*	*Int. j/g-°C*
12-7-37	1093.989	2.0054	3.0051	−.01	1.7	4,772.5	4.20719	−0.00072
12-9-37	603.781	1.9649	2.9776	−.1	2.5	2,710.7	4.20818	.00027
12-10-37	603.781	2.0051	2.9997	−.1	6.4	2,710.6	4.20802	.00011
12-14-37	603.781	1.9944	2.9979	.0	1.2	2,710.1	4.20719	−.00072
Average							4.20765	

Even temperature interval 2.0° to 3.0° C. $\Delta Z/\Delta t$=169.876 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.20791 int. j/g-°C

9-23-37	1091.161	2.4587	4.9962	0.0	2.4	11,890.7	4.20306	−0.00118
10-6-37	1092.517	2.4624	4.9935	−.3	2.4	11,905.5	4.20326	−.00098
10-8-37	1092.517	2.4981	4.9767	−.1	2.4	11,908.4	4.20432	.00008
10-14-37	1092.517	2.4990	4.9990	−.1	2.4	11,907.9	4.20414	−.00010
10-19-37	1093.647	2.5092	5.0043	−.2	2.4	11,918.8	4.20378	−.00046
10-21-37	1093.647	2.5184	5.0021	−.1	2.4	11,922.0	4.20495	.00071
10-26-37	1093.647	2.4947	5.0025	.0	2.4	11,919.6	4.20409	−.00015
10-27-37	1093.647	2.4963	5.0439	.4	2.4	11,918.4	4.20363	−.00061
10-28-37	1093.647	2.4983	4.9961	.4	2.4	11,919.6	4.20409	−.00015
11-16-37	1096.489	2.4585	5.0015	−.1	2.4	11,948.0	4.20354	−.00070
11-18-37	1096.489	2.4886	4.9970	.0	2.4	11,949.2	4.20397	−.00027
12-3-37	1093.989	2.4637	4.9717	.0	2.4	11,921.4	4.20342	−.00082
Average							4.20385	

Even temperature interval 2.5° to 5.0° C. $\Delta Z/\Delta t$=170.071 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.20424 int. j/g-°C

12-7-37	1093.989	3.0051	4.0045	0.0	1.7	4,770.4	4.20513	0.00023
12-9-37	603.781	2.9776	3.9911	−.1	2.5	2,708.8	4.20479	−.00011
12-10-37	603.781	2.9997	4.0005	−.1	6.4	2,709.1	4.20528	.00038
12-14-37	603.781	2.9979	3.9993	.0	1.2	2,709.6	4.20611	.00121
Average							4.20533	

Even temperature interval 3.0° to 4.0° C. $\Delta Z/\Delta t$=170.030 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.20490 int. j/g-°C

12-7-37	1093.989	4.0045	5.0036	0.0	1.7	4,766.4	4.20133	−0.00081
12-9-37	603.781	3.9911	5.0052	.0	2.5	2,707.6	4.20253	.00039
12-10-37	603.781	4.0005	5.0015	.0	6.4	2,707.8	4.20286	.00072
12-14-37	603.781	4.9993	4.9990	−.1	1.2	2,707.3	4.20204	−.00010
Average							4.20219	

Even temperature interval 4.0° to 5.0° C. $\Delta Z/\Delta t$=170.188 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.20214 int. j/g-°C

9-14-37	1091.161	4.9763	10.0026	1.3	4.4	23,741.4	4.19515	−0.00012
9-16-37	1091.161	5.0018	9.9480	.1	4.6	23,742.5	4.19536	.00009
9-21-37	1091.161	5.1873	9.9846	1.0	3.9	23,739.9	4.19488	−.00039
9-23-37	1091.161	4.9962	9.9910	−.4	3.7	23,743.6	4.19556	.00029
10-6-37	1092.517	4.9935	10.0029	−.6	3.7	23,771.7	4.19550	.00023
10-8-37	1092.517	4.9767	10.0084	−.2	3.7	23,772.9	4.19571	.00044
10-14-37	1092.517	4.9990	10.0050	−.1	3.7	23,772.5	4.19564	.00037
10-19-37	1093.647	5.0043	10.0104	−.2	3.7	23,795.6	4.19553	.00026
10-21-37	1093.647	5.0021	9.9988	.3	3.7	23,799.0	4.19615	.00088
10-26-37	1093.647	5.0025	10.0018	.0	3.7	23,797.3	4.19584	.00057
10-27-37	1093.647	5.0432	10.0077	.2	3.7	23,796.5	4.19570	.00043
10-28-37	1093.647	4.9954	9.9905	.3	3.7	23,795.9	4.19559	.00032
11-16-37	1096.489	5.0011	10.0036	−.2	3.7	23,853.3	4.19518	−.00009
11-18-37	1096.489	4.9965	10.0005	.0	3.7	23,853.9	4.19529	.00002
12-3-37	1093.989	4.9701	9.9808	.0	3.7	23,799.4	4.19491	−.00036
12-7-37	1093.989	5.0036	10.0067	−.3	3.7	23,798.3	4.19471	−.00056
12-9-37	603.781	5.0052	10.0755	.0	5.4	13,516.1	4.19445	−.00082
12-10-37	603.781	5.0015	10.0029	−.1	13.8	13,517.3	4.19485	−.00042
12-14-37	603.781	4.9990	9.9994	−.3	2.6	13,516.9	4.19472	−.00055
Average							4.19530	

Even temperature interval 5° to 10° C. $\Delta Z/\Delta t$=170.687 int. j/° C. Formulated value of $\Delta\alpha/\Delta t$=4.19527 int. j/g-°C

TABLE 3.—*Principal data from large-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/g-°C*	*Int. j/g-°C*
9-14-37	1091.161	10.0026	15.0032	0.9	3.9	23,697.0	4.18619	−0.0006
9-16-37	1091.161	9.9480	14.9471	−.1	3.7	23,699.1	4.18658	−.0002
9-21-37	1091.161	9.9846	15.0031	1.3	4.1	23,699.9	4.18672	−.0000
9-23-37	1091.161	9.9910	14.9987	−.5	3.7	23,701.9	4.18709	.0003
10-6-37	1092.517	10.0029	15.0069	.1	3.7	23,728.9	4.18684	.0000
10-8-37	1092.517	10.0084	15.0045	−.3	3.7	23,730.5	4.18713	.0003
10-13-37	1092.517	10.0020	15.0123	−.2	3.7	23,724.7	4.18607	−.0007
10-14-37	1092.517	10.0050	15.0064	.0	3.7	23,729.6	4.18696	.0001
10-19-37	1093.647	10.0104	15.0098	−.1	3.7	23,752.1	4.18675	−.0002
10-21-37	1093.647	9.9988	14.9970	.3	3.7	23,753.9	4.18708	.0001
10-26-37	1093.647	10.0018	15.0000	.0	3.7	23,754.5	4.18719	.0004
10-27-37	1093.647	10.0077	15.0024	.0	3.7	23,755.2	4.18732	.0004
10-28-37	1093.647	9.9905	14.9997	.0	3.7	23,755.1	4.18730	.0003
11-16-37	1096.489	10.0036	14.9993	.0	3.7	23,808.8	4.18624	−.0006
11-18-37	1096.489	9.9999	15.0004	.0	3.7	23,810.4	4.18654	−.0003
12-3-37	1093.989	9.9808	14.9891	−.1	3.7	23,757.9	4.18650	−.0002
12-7-37	1093.989	10.0067	15.0097	.0	3.7	23,754.8	4.18594	−.0008
12-9-37	603.781	10.0755	15.1357	−.3	8.9	13,496.4	4.18644	−.0004
12-10-37	603.781	10.0004	15.0065	−.3	23.0	13,494.7	4.18587	−.0010
12-14-37	603.781	9.9996	15.0019	−.2	4.3	13,497.7	4.18687	.0000
Average							4.18668	

Even temperature interval 10° to 15° C. $\Delta Z/\Delta t$=171.588 int. j/° C. Formulated value of $\Delta\alpha/\Delta t$=4.1867 int. j/g-°C

9-16-37	1091.161	14.9471	19.8801	0.0	3.7	23,675.9	4.18140	0.0002
9-21-37	1091.161	15.0031	20.0047	−.2	3.7	23,673.5	4.18096	−.0002
9-23-37	1091.161	14.9987	19.9959	−.4	3.7	23,675.9	4.18140	.0002
10-6-37	1092.517	15.0069	20.0025	.0	3.7	23,704.0	4.18135	.0001
10-8-37	1092.517	15.0045	20.0133	−.2	3.7	23,705.6	4.18165	.0004
10-13-37	1092.517	15.0123	19.9903	.0	3.7	23,705.3	4.18159	.0004
10-14-37	1092.517	15.0064	20.0082	−.1	3.7	23,704.5	4.18145	.0002
10-19-37	1093.647	15.0098	20.0137	.2	3.7	23,728.5	4.18151	.0002
10-21-37	1093.647	14.9970	19.9951	.0	3.7	23,729.6	4.18171	.0005
10-26-37	1093.647	15.0000	20.0426	.0	4.4	23,725.3	4.18093	−.0002
10-27-37	1093.647	15.0024	19.9990	.1	3.7	23,730.5	4.18188	.0006
10-28-37	1093.647	14.9997	20.0012	.1	3.7	23,730.9	4.18195	.0007
11-16-37	1096.489	14.9993	20.0001	−.1	3.7	23,784.3	4.18085	−.0003
11-18-37	1096.489	15.0004	20.0018	.0	3.7	23,785.8	4.18113	−.0000
12-3-37	1093.989	14.9891	19.9982	−.2	3.7	23,732.0	4.18085	−.0003
12-7-37	1093.989	15.0097	20.0096	.0	3.7	23,732.2	4.18088	−.0003
12-9-37	603.781	15.1357	19.9751	−.2	5.4	13,485.8	4.18125	.0000
12-10-37	603.781	15.0065	20.0009	.4	13.8	13,485.5	4.18115	−.0001
12-14-37	603.781	15.0025	20.4957	.2	2.7	13,484.5	4.18082	−.0003
Average							4.18130	

Even temperature interval 15° to 20° C. $\Delta Z/\Delta t$=172.600 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.1819 int. j/g-°C

9-16-37	1091.161	19.8801	24.9932	−0.2	3.7	23,657.6	4.17700	−0.0005
9-21-37	1091.161	20.0047	25.0045	−.7	3.7	23,658.5	4.17716	−.0003
9-23-37	1091.161	19.9959	24.9938	−.3	3.7	23,659.5	4.17735	−.0001
10-6-37	1092.517	20.0025	25.0089	0	3.7	23,686.6	4.17712	−.0004
10-8-37	1092.517	20.0133	25.0031	−.1	3.7	23,689.1	4.17758	.0005
10-13-37	1092.517	19.9903	24.9999	0	3.7	23,687.0	4.17720	−.0003
10-14-37	1092.517	20.0082	25.0133	0	3.7	23,687.8	4.17734	−.0002
10-19-37	1093.647	20.0137	24.9982	.2	3.7	23,713.5	4.17773	.0002
10-21-37	1093.647	19.9951	24.9970	−.1	3.7	23,710.6	4.17720	−.0003
10-26-37	1093.647	20.0426	25.0031	0	3.7	23,713.9	4.17780	.0003
10-27-37	1093.647	19.9990	25.0024	.1	3.7	23,713.6	4.17775	.0002
10-28-37	1093.647	20.0012	25.0023	.2	3.7	23,714.9	4.17798	.0004
11-16-37	1096.489	20.0001	25.0008	−.1	3.7	23,768.8	4.17699	−.0005
11-18-37	1096.489	20.0018	25.0001	0	3.7	23,770.8	4.17735	−.0001
12-3-37	1093.989	19.9982	25.0048	−.1	3.7	23,716.6	4.17699	−.0005
12-7-37	1093.989	20.0096	25.0079	0	3.7	23,716.1	4.17690	−.0006
12-9-37	603.781	19.9751	25.0376	−.3	5.4	13,478.4	4.17691	−.0006
12-10-37	603.781	20.0009	25.0050	0	13.8	13,477.9	4.17675	−.0007
Average							4.17728	

Even temperature interval 20° to 25° C. $\Delta Z/\Delta t$=173.739 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.1775 int. j/g-°C

TABLE 3.—*Principal data from large-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/g-°C*	*Int. j/g-°C*
9-16-37	1091.161	24.9932	29.9906	−0.1	3.7	23,655.1	4.17537	0.00024
9-21-37	1091.161	25.0045	29.9953	−.9	3.7	23,655.3	4.17540	.00027
9-23-37	1091.161	24.9938	29.9913	−.1	3.7	23,656.1	4.17554	.00041
10-6-37	1092.517	25.0089	29.9926	−.1	3.7	23,683.9	4.17546	.00033
10-8-37	1092.517	25.0031	30.0106	−.1	3.7	23,685.8	4.17581	.00068
10-13-37	1092.517	24.9999	30.0000	0	3.7	23,684.0	4.17548	.00035
10-14-37	1092.517	25.0133	30.0068	.1	3.7	23,683.4	4.17537	.00024
10-19-37	1093.647	24.9982	30.0054	0	3.7	23,706.9	4.17535	.00022
10-21-37	1093.647	24.9970	29.9945	.3	3.7	23,709.6	4.17584	.00071
10-26-37	1093.647	25.0031	29.9981	0	3.7	23,709.0	4.17573	.00060
10-27-37	1093.647	25.0024	30.0028	.2	3.7	23,710.0	4.17592	.00079
10-28-37	1093.647	25.0023	30.0017	−.1	3.7	23,709.4	4.17581	.00068
11-16-37	1096.489	25.0008	30.0012	−.1	3.7	23,764.4	4.17502	−.00011
11-18-37	1096.489	25.0001	30.0015	0	3.7	23,765.4	4.17519	.00006
11-19-37	1096.489	24.9997	30.0644	−.1	3.1	23,764.6	4.17505	−.00008
12-3-37	1093.989	25.0048	30.0131	0	3.7	23,712.6	4.17509	−.00004
12-7-37	1093.989	25.0079	30.0051	−.1	3.7	23,711.0	4.17480	−.00033
12-9-37	603.781	25.0376	29.9672	−.1	5.4	13,479.1	4.17502	−.00011
12-10-37	603.781	25.0050	30.0028	.1	13.8	13,479.7	4.17522	.00009
12-14-37	603.781	25.0430	30.0016	−.2	4.3	13,479.2	4.17506	−.00007
Average							4.17538	

Even temperature interval 25° to 30° C. $\Delta Z/\Delta t$=175.025 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17513 int. j/g-°C

9-16-37	1091.161	29.9906	39.9768	−0.5	6.1	47,308.5	4.17313	0.00006
9-21-37	1091.161	29.9953	39.9841	−1.9	6.1	47,314.3	4.17366	.00059
9-23-37	1091.161	29.9913	39.9938	−0.2	6.1	47,309.7	4.17324	.00017
10-6-37	1092.517	29.9926	39.9994	.0	6.1	47,365.0	4.17312	.00005
10-8-37	1092.517	30.0106	40.0110	−.1	6.3	47,368.8	4.17347	.00040
10-13-37	1092.517	30.0000	39.9973	.1	6.1	47,366.4	4.17325	.00018
10-14-37	1092.517	30.0068	39.9938	.0	6.1	47,364.7	4.17310	.00003
10-19-37	1093.647	30.0054	40.0252	.4	6.1	47,413.2	4.17322	.00015
10-21-37	1093.647	29.9945	40.4984	.7	6.3	47,411.3	4.17305	−.00002
10-28-37	1093.647	30.0017	40.0038	.3	6.1	47,412.4	4.17315	.00008
11-16-37	1096.489	30.0012	40.0003	.0	6.1	47,525.0	4.17260	−.00047
11-18-37	1096.489	30.0015	40.0054	.1	6.1	47,529.0	4.17296	−.00011
11-19-37	1096.489	30.0659	40.0052	.5	6.1	47,526.2	4.17271	−.00036
12-3-37	1093.989	30.0131	40.0228	.0	6.1	47,422.7	4.17278	−.00029
12-7-37	1093.989	30.0051	40.0159	−.2	6.1	47,420.5	4.17258	−.00049
12-9-37	603.781	29.9672	40.0050	.1	8.9	26,967.2	4.17275	−.00032
12-10-37	603.781	30.0028	40.0067	.1	23.0	26,967.4	4.17279	−.00028
12-14-37	603.781	30.0016	40.0000	.0	4.3	26,967.6	4.17282	−.00025
Average							4.17302	

Even temperature interval 30° to 40° C. $\Delta Z/\Delta t$=177.291 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17307 int. j/g-° C

9-16-37	1091.161	39.9768	49.9916	−0.3	6.1	47,330.3	4.17174	0.00000
9-21-37	1091.161	39.9841	49.9863	−2.4	6.1	47,325.2	4.17127	−.00047
9-23-37	1091.161	39.9938	49.9831	−0.4	6.3	47,331.9	4.17189	.00015
10-6-37	1092.517	39.9994	50.0157	−.2	6.1	47,387.6	4.17181	.00007
10-8-37	1092.517	40.0110	50.0230	−.1	6.1	47,390.1	4.17204	.00030
10-13-37	1092.517	39.9973	50.0000	.0	6.1	47,386.8	4.17173	−.00001
10-14-37	1092.517	39.9938	50.0149	−.1	6.1	47,387.0	4.17175	.00001
10-19-37	1093.647	40.0252	49.9521	.3	6.1	47,433.4	4.17168	−.00006
10-21-37	1093.647	40.4984	49.9933	.5	5.9	47,435.8	4.17190	.00016
10-28-37	1093.647	40.0038	50.0085	.4	6.1	47,439.7	4.17226	.00052
11-16-37	1096.489	40.0003	50.0032	.0	6.1	47,548.0	4.17132	−.00042
11-18-37	1096.489	40.0054	49.9958	.0	6.1	47,551.4	4.17163	−.00011
11-19-37	1096.489	40.0052	50.0046	.3	6.1	47,549.8	4.17149	−.00025
11-20-37	1096.489	40.0003	50.0006	.4	6.1	47,549.7	4.17148	−.00026
12-3-37	1093.989	40.0228	50.0059	−.2	6.1	47,444.5	4.17139	−.00035
12-7-37	1093.989	40.0108	50.0111	.1	6.1	47,444.9	4.17143	−.00031
12-9-37	603.781	40.0050	49.9467	.1	8.9	26,997.3	1.17161	−.00013
12-10-37	603.781	40.0067	50.0083	−.1	23.0	26,996.2	4.17143	−.00031
12-14-37	603.781	40.0026	50.0011	−.2	7.0	26,997.2	4.17160	−.00014
Average							4.17165	

Even temperature interval 40° to 50° C. $\Delta Z/\Delta t$=180.989 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4,17174 int. j/g-°C

TABLE 3.—*Principal data from large-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/g-°C*	*Int. j/g-°C*
9-16-37	1091.161	49.9916	59.9913	−0.1	6.1	47,375.0	4.17156	0.00032
9-21-37	1091.161	49.9863	59.9896	−1.9	6.1	47,374.8	4.17154	.00030
9-23-37	1091.161	49.9831	59.9923	−0.1	6.1	47,377.2	4.17176	.00052
10-6-37	1092.517	50.0157	60.0047	.0	6.1	47,432.1	4.17161	.00037
10-8-37	1092.517	50.0230	60.0065	−.2	6.1	47,434.1	4.17179	.00055
10-14-37	1092.517	50.0149	59.9958	.0	6.1	47,430.2	4.17143	.00019
10-19-37	1093.647	49.9521	59.9329	.3	6.1	47,477.8	4.17147	.00023
10-21-37	1093.647	49.9933	59.9976	.7	6.1	47,477.7	4.17146	.00022
10-28-37	1093.647	50.0085	60.0019	.4	6.1	47,482.4	4.17189	.00065
11-16-37	1096.489	50.0032	60.0024	.0	6.1	47,590.1	4.17090	−.00034
11-18-37	1096.489	49.9958	60.0050	−.1	6.1	47,594.8	4.17133	.00009
11-19-37	1096.489	50.0046	60.0081	.2	6.1	47,592.3	4.17110	−.00014
11-20-37	1096.489	50.0006	60.0114	.4	6.1	47,590.7	4.17096	−.00028
12-4-37	1093.989	50.0006	60.0322	.1	6.1	47,485.3	4.17086	−.00038
12-7-37	1093.989	50.0143	60.0080	−.1	6.1	47,487.5	4.17106	−.00018
12-9-37	603.781	49.9513	59.9329	−.2	8.9	27,040.3	4.17100	−.00024
12-10-37	603.781	50.0083	59.9993	.2	23.0	27,038.1	4.17063	−.00061
12-14-37	603.781	50.0009	59.9980	−.5	5.0	27,042.4	4.17135	.00011
Average							4.17132	

Even temperature interval 50° to 60° C. $\Delta Z/\Delta t$=185.663 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17124 int. j/g-°C

9-16-37	1091.161	59.9913	69.9814	0.2	6.1	47,429.1	4.17114	0.00063
9-21-37	1091.161	59.9896	70.9984	−2.1	6.8	47,431.6	4.17137	.00026
9-23-37	1091.161	59.9923	69.9831	0.1	6.1	47,432.4	4.17145	.00034
10-6-37	1092.517	60.0047	70.0140	−.2	6.1	47,488.7	4.17142	.00031
10-8-37	1092.517	60.0065	70.0097	.0	6.1	47,491.3	4.17166	.00055
10-19-37	1093.647	59.9329	70.0336	.0	6.1	47,533.0	4.17116	.00005
10-21-37	1093.647	59.9976	69.9959	.3	6.1	47,535.5	4.17139	.00028
10-28-37	1093.647	60.0019	70.0089	−.1	6.1	47,538.1	4.17163	.00052
11-16-37	1096.489	60.0024	70.0021	.0	6.1	47,648.1	4.17085	−.00026
11-18-37	1096.489	60.0050	70.0038	−.2	6.1	47,654.0	4.17139	.00028
11-19-37	1096.489	60.0081	70.0056	.0	6.1	47,656.3	4.17160	.00049
11-20-37	1096.489	60.0114	70.0042	.4	6.1	47,649.5	4.17098	−.00013
12-3-37	1093.989	60.0104	70.0119	.0	6.1	47,547.4	4.17118	.00007
12-4-37	1093.989	60.0320	70.0076	.0	6.1	47,544.7	4.17093	−.00018
12-7-37	1093.989	60.0079	70.0183	.1	6.1	47,551.1	4.17151	.00040
12-9-87	603.781	59.9329	69.9511	−.3	8.9	27,098.0	4.17085	−.00026
12-10-37	603.781	59.9993	69.9990	.3	23.0	27,095.9	4.17050	−.00061
Average							4.17124	

Even temperature interval 60° to 70° C. $\Delta Z/\Delta t$=191.520 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17111 int. j/g-°C

9-16-37	1091.161	69.9814	79.9916	0.0	6.1	47,504.6	4.17140	0.00026
9-21-37	1091.161	71.0327	80.0364	−.4	6.1	47,493.5	4.17038	−.00076
9-23-37	1091.161	69.9831	80.0028	.1	6.6	47,500.3	4.17101	−.00013
10-8-37	1092.517	70.0097	80.0089	.1	6.1	47,564.2	4.17168	.00054
10-19-37	1093.647	70.0336	80.0126	.2	6.1	47,607.4	4.17132	.00018
10-21-37	1093.647	69.9959	80.0016	.2	6.1	47,607.1	4.17129	.00015
11-16-37	1096.489	70.0021	80.0031	.0	6.1	47,721.0	4.17087	−.00027
11-18-37	1096.489	70.0038	80.0038	−.1	6.1	47,726.5	4.17137	.00023
11-19-37	1096.489	70.0056	80.0038	.0	6.1	47,721.2	4.17086	−.00028
11-20-37	1096.489	70.0042	79.9993	.2	6.1	47,722.4	4.17099	−.00015
12-3-37	1093.989	70.0119	80.0090	−.2	6.1	47,621.7	4.17132	.00018
12-4-37	1093.989	70.0076	80.0145	.0	6.1	47,615.5	4.17075	−.00039
12-7-37	1093.989	70.0183	80.0040	−.1	6.1	47,616.1	4.17081	−.00033
12-9-37	603.781	69.9511	79.9741	−.4	8.9	27,172.5	4.17114	.00000
12-10-37	603.781	69.9990	80.0085	.3	23.0	27,168.9	4.17054	−.00060
Average							4.17105	

Even temperature interval 70° to 80° C. $\Delta Z/\Delta t$=198.795 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17114 int. j/g-°C

TABLE 3.—*Principal data from large-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta\alpha/\Delta t$	Deviation from formulation
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/g-°C*	*Int. j/g-°C*
9-16-37	1091.161	79.9916	89.9950	0.0	6.1	47,597.1	4.17167	0.00043
9-21-37	1091.161	80.0364	89.9882	−.5	6.1	47,592.5	4.17125	.00001
9-23-37	1091.161	80.0028	89.9957	−.4	6.3	47,592.2	4.17123	−.00001
10-19-37	1093.647	80.0126	90.0150	.2	6.1	47,696.4	4.17127	.00003
10-21-37	1093.647	80.0016	89.9994	.0	6.1	47,698.2	4.17144	.00020
10-28-37	1093.647	79.9989	89.9751	.4	6.1	47,703.6	4.17193	.00069
11-16-37	1096.489	80.0031	90.0029	.0	6.1	47,809.8	4.17080	−.00044
11-18-37	1096.489	80.0038	90.0003	−.3	6.1	47,815.6	4.17133	.00009
11-19-37	1096.489	80.0041	90.0068	−.1	6.1	47,811.9	4.17099	−.00025
11-20-37	1096.489	79.9993	90.0060	.0	6.1	47,812.9	4.17109	−.00015
12-3-37	1093.989	80.0090	90.0074	.1	6.1	47,710.4	4.17125	.00001
12-4-37	1093.989	80.0145	90.0123	.1	6.1	47,708.6	4.17108	−.00016
12-7-37	1093.989	80.0040	90.0032	.1	6.1	47,711.2	4.17132	.00008
12-9-37	603.781	79.9741	90.0319	−.4	8.9	27,263.1	4.17133	.00009
12-10-37	603.781	80.0085	90.0092	−.1	23.0	27,263.7	4.17143	.00019
Average							4.17129	

Even temperature interval 80° to 90° C. $\Delta Z/\Delta t$=207.738 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17124 int. j/g-°C

9-16-37	1091.161	89.9950	99.9843	−0.4	6.1	47,704.3	4.17152	0.00015
9-21-37	1091.161	89.9882	99.9992	.2	6.3	47,693.1	4.17049	−.00088
9-23-37	1091.161	89.9957	99.9887	−.4	6.1	47,696.9	4.17084	−.00053
10-19-37	1093.647	90.0150	100.0086	−.4	6.2	47,806.1	4.17135	−.00002
10-21-37	1093.647	89.9994	100.0027	.1	6.1	47,807.6	4.17148	.00011
11-16-37	1096.489	90.0029	100.0024	−.2	6.1	47,920.8	4.17099	−.00038
11-18-37	1096.489	90.0003	100.0037	−.3	6.1	47,927.2	4.17158	.00021
11-19-37	1096.489	90.0068	99.9942	.0	6.1	47,925.5	4.17142	.00005
11-20-37	1096.489	90.0060	100.0045	−.3	6.1	47,921.9	4.17110	−.00027
12-3-37	1093.989	90.0074	100.0098	−.3	6.1	47,820.7	4.17138	.00001
12-4-37	1093.989	90.0123	100.0076	−.2	6.1	47,828.1	4.17205	.00068
12-9-37	603.781	90.0319	100.0076	−.3	8.9	27,371.6	4.17126	−.00011
12-10-37	603.781	90.0248	100.0075	.1	23.0	27,369.9	4.17098	−.00039
Average							4.17126	

Even temperature interval 90° to 100° C. $\Delta Z/\Delta t$=218.626 int. j/°C. Formulated value of $\Delta\alpha/\Delta t$=4.17137 int. j/g-°C

TABLE 4.—*Principal data from small-mass heat-capacity experiments*

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/°C*
11-5-37	126.708	−0.0646	2.5102	−0.1	2.3	1,758.0	169.49
11-6-37	126.708	−.0401	2.5830	−.3	1.9	1,758.4	169.65
11-11-37	126.713	.0309	2.5359	−.1	1.9	1,758.5	169.67
11-12-37	126.713	.0045	2.5027	−.2	1.9	1,758.3	169.59
11-23-37	126.842	.0321	2.6038	.5	3.7	1,760.5	169.93
11-24-37	126.842	−.0182	2.5545	.8	5.4	1,759.8	169.65
11-30-37	126.842	.0069	2.5444	.2	3.5	1,758.8	169.25
11-30-37	126.842	.0896	2.3173	.6	2.5	1,760.3	169.85
Average							169.64

Even temperature interval 0.0° to 2.5° C. $\Delta\alpha/\Delta t$=4.21210 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=169.69 int. j/° C

11-5-37	126.708	2.5111	5.0085	0.0	1.9	1,756.2	169.77
11-6-37	126.708	2.5430	5.0009	−.2	1.9	1,757.3	170.21
11-11-37	126.713	2.5368	4.9962	−.2	1.9	1,757.1	170.11
11-12-37	126.713	2.5030	4.9980	−.2	1.9	1,756.8	169.99
11-23-37	126.842	2.6240	4.9988	.6	3.7	1,758.7	170.21
11-24-37	126.842	2.5754	5.0040	.5	2.5	1,757.4	169.69
11-30-37	126.842	2.3173	5.0053	−.2	2.5	1,758.3	170.05
Average							170.00

Even temperature interval 2.5° to 5.0° C. $\Delta\alpha/\Delta t$=4.20424 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=170.07 int. j/°C

TABLE 4.—*Principal data from small-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/°C*
9-27-37	127.140	5.0941	9.5974	−0.3	5.0	3,519.3	170.47
9-28-37	127.140	5.0468	10.0059	.1	4.2	3,520.3	170.67
9-29-37	127.140	5.0469	10.0019	−.2	4.2	3,520.6	170.73
9-30-37	127.140	4.9889	10.0055	.0	4.2	3,520.0	170.61
10-1-37	127.140	5.0698	9.9952	−.2	4.2	3,519.3	170.47
11-5-37	126.708	5.0086	10.0132	−.2	2.9	3,510.6	170.55
11-6-37	126.708	5.0013	9.9995	−.3	2.9	3,511.9	170.81
11-11-37	126.713	4.9966	10.0060	−.5	2.9	3,511.4	170.68
11-12-37	126.713	4.9985	10.0012	−.4	2.9	3,511.3	170.66
11-24-37	126.842	5.0065	10.0022	.4	3.8	3,513.0	170.46
11-30-37	126.842	5.0053	10.0091	−.2	3.8	3,514.1	170.68
Average							170.61

Even temperature interval 5° to 10° C. $\Delta\alpha/\Delta t = 4.19527$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t = 170.69$ int. j/°C

9-27-37	127.140	9.5974	15.0994	−0.3	4.5	3,520.3	171.75
9-28-37	127.140	10.0059	15.0066	−.3	4.2	3,519.0	171.49
9-29-37	127.140	10.0019	15.0031	−.1	4.2	3,519.1	171.51
9-30-37	127.140	10.0055	15.0155	−.4	4.2	3,518.9	171.47
10-1-37	127.140	9.9952	15.1422	.1	4.2	3,518.4	171.37
11-5-37	126.708	10.0132	15.0025	−.2	2.9	3,510.0	171.50
11-6-37	126.708	9.9995	15.0001	−.3	2.9	3,511.1	171.72
11-11-37	126.713	10.0131	14.9993	−.4	2.9	3,510.9	171.66
11-12-37	126.713	10.0012	15.0015	−.2	2.9	3,510.5	171.58
11-24-37	126.842	10.0022	15.0063	−.3	3.9	3,512.1	171.36
11-30-37	126.842	10.0091	15.0004	−.2	3.8	3,513.1	171.56
Average							171.54

Even temperature interval 10° to 15° C. $\Delta\alpha/\Delta t = 4.18678$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t = 171.59$ int. j/°C

9-27-37	127.140	15.0994	20.0230	−0.4	4.3	3,521.2	172.64
9-28-37	127.140	15.0066	19.9974	−.3	4.3	3,520.6	172.52
9-29-37	127.140	15.0031	20.0028	−.2	4.3	3,521.0	172.60
9-30-37	127.140	15.0155	19.9961	−.3	4.3	3,520.7	172.54
10-1-37	127.140	15.1422	20.0015	−.1	4.2	3,519.3	172.26
11-5-37	126.708	15.0025	20.0054	−.3	3.0	3,512.0	172.61
11-6-37	126.708	15.0001	20.0011	−.3	3.0	3,512.7	172.75
11-11-37	126.713	14.9993	20.0015	−.4	3.0	3,512.7	172.73
11-12-37	126.713	15.0015	20.0013	−.2	3.0	3,512.4	172.67
11-24-37	126.842	15.0063	20.0075	−.1	3.8	3,514.1	172.47
11-30-37	126.842	15.0004	19.9991	−.3	3.8	3,514.4	172.53
Average							172.57

Even temperature interval 15° to 20° C. $\Delta\alpha/\Delta t = 4.18119$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t = 172.60$ int. j/° C

9-27-37	127.140	20.0230	24.9939	−0.2	4.6	3,524.2	173.71
9-28-37	127.140	19.9974	24.9946	−.3	4.3	3,523.7	173.61
9-29-37	127.140	20.0028	24.9979	−.4	4.3	3,524.3	173.73
9-30-37	127.140	19.9961	24.9962	−.2	4.3	3,524.0	173.67
10-1-37	127.140	20.0015	25.0055	−.4	4.3	3,522.8	173.43
11-5-37	126.708	20.0054	25.0067	−.3	3.0	3,514.9	173.65
11-6-37	126.708	20.0011	24.9988	−.3	3.0	3,515.6	173.79
11-11-37	126.713	20.0015	24.9971	−.3	3.0	3,515.8	173.81
11-12-37	126.713	20.0013	24.9966	−.2	3.0	3,515.4	173.73
11-24-37	126.842	20.0075	25.0031	−.2	3.9	3,517.2	173.55
11-30-37	126.842	19.9991	24.9978	−.4	3.9	3,517.4	173.59
Average							173.66

Even temperature interval 20° to 25° C. $\Delta\alpha/\Delta t = 4.17753$ int. j/g-°C
Formulated value of $\Delta Z/\Delta t = 173.74$ int. j/°C

TABLE 4.—*Principal data from small-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j/°C*
9-27-37	127.140	24.9939	29.9932	−0.2	4.3	3,530.2	175.21
9-28-37	127.140	24.9946	29.9991	−.1	4.3	3,529.3	175.03
9-29-37	127.140	24.9979	29.9949	−.3	4.3	3,529.2	175.01
9-30-37	127.140	24.9962	29.9948	−.2	4.3	3,529.8	175.13
10-1-37	127.140	25.0058	30.0080	−.4	4.3	3,528.9	174.95
11-5-37	126.708	25.0067	30.0113	−.2	3.0	3,520.1	175.00
11-8-37	126.708	24.9988	29.9981	−.2	3.0	3,520.5	175.08
11-11-37	126.713	24.9971	29.9968	−.2	3.0	3,521.0	175.16
11-12-37	126.713	24.9966	29.9974	−.2	3.0	3,520.4	175.04
11-24-37	126.842	25.0031	30.0057	−.2	3.9	3,522.4	174.90
11-29-37	126.842	25.0033	29.9767	−.3	4.2	3,523.0	175.02
Average							175.05

Even temperature interval 25° to 30° C. $\Delta\alpha/\Delta t$=4.17513 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=175.02 int. j/°C

9-27-37	127.140	29.9932	39.9929	−0.5	7.3	7,078.8	177.32
9-28-37	127.140	29.9991	39.9917	−.1	7.3	7,078.1	177.25
9-29-37	127.140	29.9949	39.9848	−.4	7.3	7,079.1	177.35
9-30-37	127.140	29.9948	39.9923	−.6	7.3	7,078.4	177.27
10-1-37	127.140	30.0080	39.9991	−.9	7.3	7,078.1	177.25
11-5-37	126.708	30.0117	40.0274	−.2	5.2	7,059.9	177.23
11-8-37	126.708	29.9930	39.9952	−.1	5.2	7,059.2	177.16
11-11-37	126.713	29.9968	39.9884	−.5	5.2	7,061.5	177.37
11-12-37	126.713	29.9974	39.9950	−.3	5.2	7,059.7	177.19
11-24-37	126.842	30.0057	40.0131	−.3	6.6	7,064.5	177.13
11-29-37	126.842	29.9797	40.0490	−.7	6.6	7,065.1	177.19
Average							177.25

Even temperature interval 30° to 40° C. $\Delta\alpha/\Delta t$=4.17307 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=177.29 int. j/°C

9-27-37	127.140	39.9929	49.9881	−0.6	7.5	7,115.4	181.14
9-28-37	127.140	39.9917	50.0028	−.5	7.5	7,113.2	180.92
9-29-37	127.140	39.9848	50.0068	−.5	7.5	7,114.9	181.09
9-30-37	127.140	39.9923	50.0015	−.6	7.5	7,113.3	180.93
10-1-37	127.140	39.9991	50.0037	−.7	7.5	7,114.2	181.02
11-5-37	126.708	40.0274	50.0222	−.3	5.3	7,095.7	180.98
11-8-37	126.708	39.9952	49.9983	−.2	5.3	7,095.1	180.92
11-11-37	126.713	39.9967	49.9975	−.3	5.3	7,095.5	180.94
11-12-37	126.713	40.0046	50.0032	−.4	5.3	7,094.4	180.83
11-24-37	126.842	40.0231	50.0078	−.3	6.7	7,099.9	180.84
11-29-37	126.842	40.0490	50.0050	−.4	6.7	7,100.5	180.90
Average							180.96

Even temperature interval 40° to 50° C. $\Delta\alpha/\Delta t$=4.17174 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=180.99 int. j/°C

9-27-37	127.140	49.9881	59.9833	−0.7	7.6	7,160.4	185.71
9-28-37	127.140	50.0028	59.9990	−.8	7.6	7,159.4	185.61
9-29-37	127.140	50.0068	59.9980	−.3	7.6	7,159.9	185.66
9-30-37	127.140	50.0015	60.0036	.1	7.6	7,159.9	185.66
10-1-37	127.140	50.0037	60.0053	−.7	7.6	7,160.1	185.68
11-5-37	126.708	50.0222	60.0165	−.2	5.4	7,142.6	185.73
11-8-37	126.708	49.9983	59.9981	−.5	5.4	7,141.6	185.63
11-11-37	126.713	49.9975	59.9969	−.6	5.4	7,142.2	185.67
11-12-37	126.713	50.0032	59.9945	−.1	5.4	7,141.1	185.56
11-24-37	126.842	50.0225	60.0085	−.2	6.9	7,145.8	185.49
11-29-37	126.842	50.0050	60.0022	−.3	6.8	7,146.1	185.52
Average							185.63

Even temperature interval 50° to 60° C. $\Delta\alpha/\Delta t$=4.17124 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=185.66 int. j/°C

TABLE 4.—*Principal data for small-mass heat-capacity experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Pump energy	Energy for even temperature interval	$\Delta Z/\Delta t$
	g	°C	°C	*Int. j*	*Int. j*	*Int. j*	*Int. j*/°C
9-27-37	127.140	59.9833	69.9959	−1.1	7.7	7,219.3	191.61
9-28-37	127.140	59.9990	69.9834	−1.0	7.7	7,218.1	191.49
9-29-37	127.140	59.9980	69.9870	−0.2	7.7	7,217.9	191.47
9-30-37	127.140	60.0036	70.0132	−0.2	8.0	7,217.0	191.38
10-1-37	127.140	60.0053	69.9886	−1.1	7.7	7,218.7	191.53
11-5-37	126.708	60.0165	70.0135	−0.3	5.6	7,200.8	191.37
11-8-37	126.708	59.9973	70.0845	−.3	5.6	7,199.2	191.41
11-12-37	126.713	59.9945	69.9967	−.4	5.6	7,200.0	191.47
11-24-37	126.842	60.0085	69.9908	−.4	7.0	7,204.5	191.38
11-29-37	126.842	60.0022	69.9523	−.4	7.0	7,204.8	191.41
Average							191.47

Even temperature interval 60° to 70° C. $\Delta\alpha/\Delta t$=4.17111 int. j/g-°C
Formulated value at $\Delta Z/\Delta t$=191.52 int. j/°C

9-27-37	127.140	69.9959	79.9973	−1.2	7.8	7,292.0	198.88
9-28-37	127.140	69.9834	80.0011	−.5	7.8	7,291.1	198.79
9-29-37	127.140	69.9870	80.0073	−.3	7.8	7,290.8	198.76
9-30-37	127.140	70.0132	80.0058	−.2	8.8	7,289.9	198.67
10-1-37	127.140	69.9886	80.0043	−.6	7.8	7,291.5	198.83
11-5-37	126.708	70.0135	80.0056	−.1	5.7	7,273.6	198.84
11-8-37	126.708	70.0845	79.9952	−.4	5.7	7,272.8	198.76
11-29-37	126.842	69.9523	79.9922	−.3	7.1	7,277.7	198.69
Average							198.78

Even temperature interval 70° to 80° C. $\Delta\alpha/\Delta t$=4.17114 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=198.79 int. j/° C

9-27-37	127.140	79.9973	89.9929	−0.5	8.0	7,381.9	207.80
9-28-37	127.140	80.0011	90.0146	−.2	8.6	7,379.7	207.64
9-29-37	127.140	80.0073	90.0104	−.5	8.0	7,381.1	207.78
9-30-37	127.140	80.0058	90.0117	−.8	8.3	7,379.7	207.64
10-1-37	127.140	80.0043	89.9998	−.6	8.0	7,381.5	207.82
11-5-37	126.708	80.0056	89.9972	−.3	5.8	7,363.4	207.81
11-8-37	126.708	79.9952	90.0004	−.7	5.8	7,363.2	207.79
11-29-37	126.842	79.9922	90.0033	−.3	7.2	7,367.7	207.68
Average							207.75

Even temperature interval 80° to 90° C. $\Delta\alpha/\Delta t$=4.17124 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=207.74 int. j/° C

9-27-37	127.140	89.9929	99.9985	−0.7	8.1	7,489.8	218.63
9-28-37	127.140	90.0146	100.0007	.2	8.7	7,488.9	218.54
9-29-37	127.140	90.0104	99.9982	−.1	8.7	7,489.5	218.60
9-30-37	127.140	90.0117	99.9885	−.4	8.4	7,488.2	218.47
10-1-37	127.140	89.9998	99.9970	−.6	8.1	7,489.9	218.64
11-5-37	126.708	89.9972	99.9959	−.6	5.9	7,471.8	218.63
11-8-37	126.708	90.0004	100.0010	−.9	6.7	7,472.6	218.71
11-29-37	126.842	90.0170	100.0005	−.4	7.3	7,476.0	218.50
Average							218.59

Even temperature interval 90° to 100° C. $\Delta\alpha/\Delta t$=4.17137 int. j/g-°C
Formulated value of $\Delta Z/\Delta t$=218.61 int. j/°C

TABLE 5.—*Calculation of specific heat at 1-atmosphere pressure*

Temperature interval	$\Delta\alpha/\Delta t$, measured	Reductions to give C_p at 1 atmosphere			C_p, experimental	C_p, formulated	Deviation exp.—form.	Mid-temperature of interval
		$\frac{\Delta H}{\Delta t}-\frac{\Delta\alpha}{\Delta t}$	$\left(\frac{\Delta H}{\Delta t}\right)_{p=1}-\left(\frac{\Delta H}{\Delta t}\right)_{sat}$	$-\left(\frac{C_{p=1}}{\frac{\Delta H}{\Delta t}}\right)_{t=1}$				
1	2	3	4	5	6	7	8	9
°C	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*	*°C*
0 to 1	4.21411	0.00085	−0.00054	−0.00001	4.21441	4.21508	−0.00067	0.5
0 to 2.5	4.21267	.00089	−.00052	−.00008	4.21296	4.21242	.00054	1.25
1 to 2	4.21087	.00090	−.00051	−.00001	4.21125	4.21158	−.00033	1.5
0 to 5	4.20811	.00096	−.00051	−.00027	4.20829	4.20837	−.00008	2.5
2 to 3	4.20764	.00096	−.00051	−.00001	4.20808	4.20837	−.00029	2.5
3 to 4	4.20533	.00101	−.00050	−.00001	4.20583	4.20542	.00041	3.5
2.5 to 5.0	4.20385	.00103	−.00050	−.00006	4.20432	4.20472	−.00040	3.75
4 to 5	4.20219	.00107	−.00050	−.00001	4.20275	4.20272	.00003	4.5
5 to 10	4.19530	.00127	−.00047	−.00018	4.19592	4.19588	.00004	7.5
10 to 15	4.18668	.00167	−.00045	−.00012	4.18778	4.18784	−.00006	12.5
15 to 20	4.18130	.00217	−.00045	−.00008	4.18294	4.18280	.00014	17.5
20 to 25	4.17728	.00279	−.00045	−.00006	4.17956	4.17977	−.00021	22.5
25 to 30	4.17538	.00354	−.00047	−.00004	4.17840	4.17814	.00026	27.5
30 to 40	4.17302	.00500	−.00053	−.00010	4.17739	4.17744	−.00005	35
40 to 50	4.17165	.00761	−.00065	−.00007	4.17854	4.17866	−.00012	45
50 to 60	4.17132	.01122	−.00084	−.00006	4.18164	4.18161	.00003	55
60 to 70	4.17124	.01606	−.00110	−.00006	4.18614	4.18604	.00010	65
70 to 80	4.17105	.02239	−.00144	−.00007	4.19193	4.19200	−.00007	75
80 to 90	4.17129	.03049	−.00188	−.00008	4.19982	4.19972	.00010	85
90 to 100	4.17126	.04063	−.00241	−.00010	4.20939	4.20947	−.00008	95

TABLE 6.—*Heat capacity of air-free water at 1 atmosphere pressure*

Temperature	C_p	Enthalpy, H_t		Temperature	C_p	Enthalpy, H_t	
°C	*Abs. j/g-°C*	*Abs. j/g*	*IT Cal/g*	°C	*Abs. j/g-°C*	*Abs. j/g*	*IT Cal/g*
0	4. 2177	0. 1026	0. 0245	50	4. 1807	209. 3729	50. 0079
1	4. 2141	4. 3184	1. 0314	51	4. 1810	213. 5538	51. 0065
2	4. 2107	8. 5308	2. 0376	52	4. 1814	217. 7350	52. 0051
3	4. 2077	12. 7400	3. 0429	53	4. 1817	221. 9166	53. 0039
4	4. 2048	16. 9462	4. 0475	54	4. 1820	226. 0984	54. 0027
5	4. 2022	21. 1498	5. 0515	55	4. 1824	230. 2806	55. 0016
6	4. 1999	25. 3508	6. 0549	56	4. 1828	234. 4632	56. 0006
7	4. 1977	29. 5496	7. 0578	57	4. 1832	238. 6462	56. 9997
8	4. 1957	33. 7463	8. 0602	58	4. 1836	242. 8296	57. 9989
9	4. 1939	37. 9410	9. 0621	59	4. 1840	247. 0134	58. 9982
10	4. 1922	42. 1341	10. 0636	60	4. 1844	251. 1976	59. 9975
11	4. 1907	46. 3255	11. 0647	61	4. 1849	255. 3822	60. 9970
12	4. 1893	50. 5155	12. 0654	62	4. 1853	259. 5673	61. 9966
13	4. 1880	54. 7041	13. 0659	63	4. 1858	263. 7529	62. 9963
14	4. 1869	58. 8916	14. 0660	64	4. 1863	267. 9390	63. 9962
15	4. 1858	63. 0779	15. 0659	65	4. 1868	272. 1256	64. 9961
16	4. 1849	67. 2632	16. 0655	66	4. 1874	276. 3127	65. 9962
17	4. 1840	71. 4476	17. 0650	67	4. 1879	280. 5003	66. 9964
18	4. 1832	75. 6312	18. 0642	68	4. 1885	284. 6885	67. 9967
19	4. 1825	79. 8141	19. 0633	69	4. 1890	288. 8772	68. 9972
20	4. 1819	83. 9963	20. 0622	70	4. 1896	293. 0665	69. 9977
21	4. 1813	88. 1778	21. 0609	71	4. 1902	297. 2564	70. 9985
22	4. 1808	92. 3589	22. 0596	72	4. 1908	301. 4469	71. 9994
23	4. 1804	96. 5395	23. 0581	73	4. 1915	305. 6381	73. 0004
24	4. 1800	100. 7196	24. 0565	74	4. 1921	309. 8299	74. 0016
25	4. 1796	104. 8994	25. 0548	75	4. 1928	314. 0224	75. 0030
26	4. 1793	109. 0788	26. 0530	76	4. 1935	318. 2155	76. 0045
27	4. 1790	113. 2580	27. 0512	77	4. 1942	322. 4094	77. 0062
28	4. 1788	117. 4369	28. 0493	78	4. 1949	326. 6039	78. 0080
29	4. 1786	121. 6157	29. 0474	79	4. 1957	330. 7992	79. 0101
30	4. 1785	125. 7943	30. 0455	80	4. 1964	334. 9952	80. 0123
31	4. 1784	129. 9727	31. 0435	81	4. 1972	339. 1920	81. 0147
32	4. 1783	134. 1510	32. 0414	82	4. 1980	343. 3897	82. 0172
33	4. 1783	138. 3293	33. 0394	83	4. 1988	347. 5881	83. 0200
34	4. 1782	142. 5076	34. 0374	84	4. 1997	351. 7873	84. 0230
35	4. 1782	146. 6858	35. 0353	85	4. 2005	355. 9874	85. 0262
36	4. 1783	150. 8641	36. 0333	86	4. 2014	360. 1883	86. 0295
37	4. 1783	155. 0423	37. 0312	87	4. 2023	364. 3902	87. 0331
38	4. 1784	159. 2207	38. 0292	88	4. 2032	368. 5929	88. 0369
39	4. 1785	163. 3991	39. 0272	89	4. 2042	372. 7966	89. 0410
40	4. 1786	167. 5777	40. 0253	90	4. 2051	377. 0012	90. 0452
41	4. 1787	171. 7563	41. 0233	91	4. 2061	381. 2068	91. 0497
42	4. 1789	175. 9351	42. 0214	92	4. 2071	385. 4135	92. 0545
43	4. 1791	180. 1141	43. 0195	93	4. 2081	389. 6211	93. 0594
44	4. 1792	184. 2933	44. 0177	94	4. 2092	393. 8297	94. 0647
45	4. 1795	188. 4726	45. 0159	95	4. 2103	398. 0395	95. 0701
46	4. 1797	192. 6522	46. 0142	96	4. 2114	402. 2503	96. 0759
47	4. 1799	196. 8320	47. 0125	97	4. 2125	406. 4622	97. 0819
48	4. 1802	201. 0120	48. 0109	98	4. 2136	410. 6753	98. 0882
49	4. 1804	205. 1923	49. 0094	99	4. 2148	414. 8895	99. 0947
				100	4. 2160	419. 1049	100. 1015

TABLE 7.—*Enthalpy of saturated liquid water*

Temperature	a_0^t	β	Enthalpy		
°C	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Abs. j/g*	*IT Cal/g*
0	0. 0000	0. 0121	0. 0000	0. 0000	0. 0000
5	21. 0408	. 0169	21. 0456	21. 0496	5. 0276
10	42. 0172	. 0233	42. 0283	42. 0363	10. 0402
15	62. 9511	. 0316	62. 9706	62. 9826	15. 0431
20	83. 8571	. 0425	83. 8875	83. 9034	20. 0400
25	104. 7447	. 0564	104. 7890	104. 8089	25. 0332
30	125. 6204	. 0741	125. 6824	125. 7063	30. 0244
35	146. 4883	. 0963	146. 5725	146. 6003	35. 0149
40	167. 3511	. 1241	167. 4631	167. 4949	40. 0055
45	188. 2108	. 1583	188. 3570	188. 3928	44. 9968
50	209. 0685	. 2002	209. 2566	209. 2964	49. 9896
55	229. 9251	. 2510	230. 1640	230. 2077	54. 9842
60	250. 7810	. 3123	251. 0812	251. 1289	59. 9811
65	271. 6366	. 3858	272. 0102	272. 0619	64. 9808
70	292. 4921	. 4730	292. 9530	293. 0087	69. 9839
75	313. 3477	. 5760	313. 9116	313. 9712	74. 9907
80	334. 2035	. 6970	334. 8883	334. 9519	80. 0019
85	355. 0596	. 8381	355. 8856	355. 9532	85. 0180
90	375. 9159	1. 0019	376. 9057	376. 9773	90. 0395
95	396. 7726	1. 1909	397. 9514	398. 0270	95. 0671
100	417. 6296	1. 4082	419. 0257	419. 1053	100. 1016

V. REVIEW OF EARLIER WORK AND COMPARISONS

It is of interest to present a résumé of comparisons between the present results and the earlier results, but unfortunately, it seems impossible to make all such comparisons on the basis of definite evaluation. As mentioned above, so many uncertain factors regarding units, standards, and experimental technique have been involved in some of the earlier work that the results of much of the pioneer research is difficult to interpret and appraise in terms of present standards. In spite of the care with which these various determinations were made, the diversity of results indicates that in some of the work, the uncertainties were greater than supposed.

Since the present determinations have been made by use of the present standards of electromotive force and electric resistance, they yield values for the heat capacity of water in international electric-energy units. They are comparable, in kind, to two types of previous measurements, those in which the variation of specific heat with temperature has been observed, and those in which the heat capacity of water has been measured, either in mechanical or electrical units of energy.

Comparisons of the determinations of the variation of specific heat may be made, independently of the absolute value of the energy units. These comparisons may easily be made by arbitrarily choosing a temperature at which the observed specific heat is taken as unity. Differences in temperature scales used and such calorimetric errors as heat leaks, however, would affect the accord.

For the evaluation of the heat capacity or specific heat of water in the fundamental or absolute units of energy, the choice of values for

the relations between units and standards of different periods is involved, particularly for measurements made by the method of electric heating. The data available for this purpose are not adequate to yield satisfactory appraisals of all the experimental data. The opinions of some who have studied this matter are interesting.

For example, in the discussion of T. H. Laby's [13] critical review paper on the mechanical equivalent of heat, several physicists have given their views. F. E. Smith said that he "had little faith in the values of physical constants obtained by applying corrections long after the date of the observations." G. M. Clark said "I doubt whether much is gained by discussing the results of other observers by making known corrections that arise through the light of later knowledge * * * the halo of nebulosity surrounding any physical determination is probably greater than the original experimenter cared to acknowledge to himself. I am also of the opinion that the only person who can revise any old determination is the person who made it." Ezer Griffiths said "I view with misgivings attempts to correct old work unless made by the investigators themselves, as they alone are acquainted with all the facts concerning the apparatus." E. H. Griffiths said "I confess that it appears to me that it is the final and not the earlier conclusions of an author which should be quoted." In this very frank discussion, several authors gave reappraisals of their earlier numerical values, which are most helpful to reviewers.

In comparing various appraisals made in the past, much can be found to support these views. It seems, however, that part of the discord which has baffled reviewers may be removed by use of more complete correction data, without too ruthless rejection of early experimental work.

In accord with the above warnings of caution, the present authors propose to accept at their face values the experimenters' own reappraisals, where available. In view of the impossibility of precise interpretation and reduction to present standards of much of the earlier work, and since this service has been already so thoroughly performed by previous reviewers, a complete review will not be undertaken here. Instead, only a few of the determinations which have been cited in the past as important or authoritative have been selected for examination and correlation to indicate the extent of corroboration. In order to coordinate them for intercomparison, some reductions have been made by using equivalents or ratios which are based on more complete experimental evidence than those used in former reviews. These data will be examined in two respects, the first by considering the experimental data yielding values for the mechanical equivalent of heat, each in terms of some definite heat unit, and second, by considering data on the change of specific heat with temperature.

James Prescott Joule

Joule [14] appears to have been the first to undertake systematic measurements of the mechanical equivalent. In 1850, from experiments by a number of methods, he chose a value of 772 foot-pounds per heat unit. Later, in 1878, by water friction in a calorimeter, he obtained the value 772.6 foot-pounds per 62° F heat unit. Because these experiments belong to an early period in the development of standards of physical measurements, it is impossible to evaluate the results in terms of present standards, but their pioneer nature and

classical refinement set them apart as exempt from any purely numerical appraisal of their relative accuracy. Tribute to Joule's work is perpetuated by the use of his name to designate the unit of work.

Henry A. Rowland

Rowland [15] followed Joule by making a series of elaborate experiments similar in principle to Joule's, but with greater care and refinements in some respects. Although the thermometry of that time was less precise than later, Rowland's measurements were made and recorded so carefully that they could be revised later when the thermometers that he used had been compared with better-known standards. William S. Day [16], with Rowland's permission and advice, compared Rowland's thermometers with the Paris Standard (international hydrogen scale) and made a revision of the results 20 years after the original work.

At the conclusion of his paper, Rowland says "Between the limits of 15° and 25° C, I feel almost certain that no subsequent experiments will change my values of the equivalent so much as 2 parts in 1,000, and even outside those limits, say between 10° and 30°, I doubt whether the figures will ever be changed much more than that amount." This concluding estimate seems to have been conservative.

Table 8 gives the values reported by Rowland and the values corrected by Day at five temperatures from 10° to 30° C. It also gives the NBS values reduced to the same temperature intervals and rounded to the same number of figures. The last two columns give the deviations of Rowland's original and Day's revision from the NBS. Rowland's smoothed results differ most from the NBS at the ends of the range from 10° to 30° C, and there, by less than his estimated 2 parts in 1,000.

TABLE 8.—*Comparison of specific heat values of Rowland with NBS values*

Temperature	Rowland, 1879	Day's revision, 1898	NBS 1939	Rowland minus NBS	Day's revision minus NBS
°C	*j/g-°C*	*j/g-°C*	*j/g-°C*	*j/g-°C*	*j/g-°C*
10	4.200	4.196	4.192	0.008	0.004
15	4.189	4.188	4.186	.003	.002
20	4.179	4.181	4.182	−.003	−.001
25	4.173	4.176	4.180	−.007	−.004
30	4.171	4.174	4.179	−.008	−.005
Average				−0.0016	−0.0010

Rowland's values are greater than the NBS values in the lower part of this range and less in the upper part. It seems probable that these departures can be explained by the correction he applied for heat leak, or "radiation," as he called it. This correction amounted to over 2 percent of the energy input when the temperature of the calorimeter differed from that of the jacket by 10° C. He determined the "coefficients of radiation" by measurement, but in discussing them he says "the circumstances in the experiments are not the same as when the radiation was obtained." These circumstances, he states, "tend to give *too small* [italics Rowland's] coefficients of radiation, and this is confirmed by looking over the final tables." He, however, did not feel at liberty to make corrections on this

basis. Had these coefficients been greater by nearly 4 percent, it would have accounted for the difference in slope of Rowland's curve from that of the NBS, as will be seen by referring to table 8. At 20° C, which is the midtemperature of the range in which Rowland estimated his greatest precision, Rowland's revised value is less than the NBS value by about 1 part in 4,000. At 15° C, which was about the average jacket temperature, and where the heat leak would have been zero, Rowland's revised value is greater than the NBS value by 1 part in 2,000.

It is possible that his remarkable accord with recent determinations is accidental, but it appears more likely to be due to the thoroughness with which he is known to have worked.

Reynolds and Moorby

These workers [17] determined the mechanical equivalent of heat by means of a hydraulic brake driven by a steam engine. The measurements were carried out on an engineering scale, the power input being in some experiments as large as 65 hp. This feature has sometimes been considered an advantage as compared with lesser proportions. The heat developed was used to raise the temperature of water over a range of nearly 100° C. These distinctions give these measurements an importance for purposes of comparison.

It must be recognized that in some other respects, the apparatus and technique were less refined than in the case of some of the other determinations. Although the work is described at great length, it is difficult to ascertain all details which would aid in correlating the numerical result with others. This is the case with the record of the initial and final temperatures and pressures of the water which absorbed the energy input as sensible heat. It seems that for the final value of 4.1832 abs. j/g-°C, the approximate range of state was from a temperature of 1.3° C and a pressure of 1.53 atmospheres, to a final temperature of 100° C and a pressure of 1.43 atmospheres. The change in enthalpy for this change of state may be computed from the NBS data as follows:

Enthalpy at 1.3° C, pressure 1 atm	5. 583 abs. j/g.
Change for 0.53 atm	0. 054 abs. j/g.
Enthalpy at 1.3° C, pressure 1.53 atm	5. 637 abs. j/g.
Enthalpy at 100° C, pressure 1 atm	419. 105 abs. j/g.
Correction for 0.43 atm	0. 033 abs. j/g.
Enthalpy at 100° C, pressure 1.43 atm	419. 138 abs. j/g.
Change in enthalpy 1.3° C, 1.53 atm, to 100° C and 1.43 atm	413. 501 abs. j/g.
Change per degree by NBS value	4. 1895 abs. j/g-°C.
Reynolds and Moorby's value	4. 1832 abs. j/g-°C.
R. and M.–NBS	0. 0063 abs. j/g-°C (or 1 part in 660)

The accord of this result with the NBS result is inferior to the accord of Rowland's result after Day's revision for temperature scale. Inasmuch as the means of protection from heat leak in Reynolds and Moorby's work were less complete and the range of temperature considerably greater, it is very probable that this may account in part for the greater discrepancy. Although this extensive research suffers by comparison with modern technique, the approximate confirmation of smaller scale laboratory measurements has served for many years as a classical contribution to engineering data.

Laby and Hercus

They [18] determined the mechanical equivalent of heat by direct mechanical measurements using an induction dynamometer and the method of continuous-flow calorimetry. The ingenuity of design and refinements of technique justify their aim at "the highest precision attainable with the present developments of physical technique."

There have been two serious criticisms of Laby and Hercus' work. Birge [19] has proposed a reevaluation of their result by disregarding the experiments near 20° C on account of their large residual. In a later paper, Laby and Hercus [20] have noted this criticism and have accepted the proposal. Jessel [21] has reported finding differences in the specific heat of air-free water and air-saturated water and has questioned Laby and Hercus' result on the score that air-free water was not used. In replying to this criticism, Laby and Hercus [20] deny the validity of Jessel's conclusions in their own case and show by computation that the effect is negligible. As a reappraisal in 1935 of the final result of their measurements, Laby and Hercus give for the mechanical equivalent for both deaerated and aerated water, the value of 4.1852×10^7 ergs/15° cal, which may be taken as their appraisal of their results for purposes of comparison. The present NBS measurements give the value of 4.1858 j (abs.)/g-°C for C_p at 15° C and 1 atmosphere, which agrees within 1 part in 7,000 with Laby and Hercus' value.

Callendar and Barnes

Their work [22] on the measurement of the heat capacity of water between 5° and 95° C by the continuous electric-calorimetric method is without doubt more pretentious and comprehensive than any of the other researches on this property of water. The results which were obtained from measurements made by Barnes in 1899 and 1900 in terms of the electrical standards of that period have since been the subject of numerous reviews [13, 22, 23, 24, 25], mostly with the object of deriving better appraisals of the value of the mechanical equivalent of heat by applying corrections to bring them into accord with known standards. The diversity of these reappraisals emphasizes the difficulty and uncertainty involved. Even Callendar, who cooperated in the design and preparation of the apparatus, and Barnes, who carried out the experimental part of the program, differed in their opinions of the validity of the accounting for heat leak. It seems that for the purpose of comparisons, the best course is to take the authors' own latest estimates. These along with others are given in table 9.

In 1909 Barnes [22] revised his original figures of 1902 by applying corrections for the value of the standard cells. Callendar [26] reviewed previous experiments on the variation of specific heat of water, described experiments by a new method, and derived a formula for specific heat. It is somewhat difficult to differentiate Callendar's interpretations of these several elements, and, for purposes of comparison, it seems best to take his tabulated figures, referred to the value at 20° C as unity. Callendar later, in 1925 [13], in a discussion of T. H. Laby's paper on the Mechanical Equivalent of Heat, has given a reappraisal of the value at 20° C from the Callendar and Barnes' experiments as 4.178 abs. j/g-°C. This value is practically the same as the value 4.1785 given by Barnes in 1909. Laby's

appraisal of Callendar and Barnes' value made at the same time is 4.1795 at 20° C. The NBS value for 20° C at present is 4.1819, which is about 1 part in 1,200 greater than Barnes' figure. Barnes' estimated values of the specific heats at other temperatures deviate from the NBS values by as much as 1 in 500, while Callendar's estimate is for the most part within 1 part in 1,000 of the NBS value. Barnes' mean value between 5° and 95° C of 4.1835 is about 1 part in 1,000 less than the corresponding mean value of 4.1877 from the NBS measurements.

TABLE 9.—*Comparison of specific heat value of Callendar and Barnes with NBS value*

Temperature	Barnes original 1902	Barnes revised 1909	Callendar revised 1925	Laby's revision of Callendar and Barnes 1925	Callendar 1912	Barnes 1909	NBS 1939
°C	*Abs.j/g-°C*	*Abs.j/g-°C*	*Abs.j/g-°C*	*Abs.j/g-°C*	cal_{20}/g-°C	cal_{20}/g-°C	cal_{20}/g-°C
0							1.0087
5	4.2105	4.2052			1.00596	1.00639	1.0068
10	4.1979	4.1926			1.00310	1.00337	1.0024
15	4.1895	4.1842			1.00122	1.00136	1.0009
20	4.1838	4.1785	4.178	4.1795	1.00000	1.00000	1.0000
25	4.1801	4.1748			0.99922	0.99911	0.9994
30	4.1780	4.1727			.99877	.99861	.9991
35	4.1773	4.1720			.99856	.99844	.9991
40	4.1773	4.1720			.99856	.99844	.9992
45	4.1782	4.1729			.99871	.99866	.9994
50	4.1798	4.1745			.99901	.99904	.9997
55	4.1819	4.1766			.99942	.99955	1.0001
60	4.1845	4.1792			.99994	1.00017	1.0006
65	4.1870	4.1817			1.00055	1.00077	1.0011
70	4.1898	4.1845			1.00125	1.00144	1.0018
75	4.1925	4.1872			1.00201	1.00208	1.0026
80	4.1954	4.1901			1.00288	1.00278	1.0034
85	4.1982	4.1929			1.00380	1.00345	1.0044
90	4.2010	4.1957			1.00479	1.00412	1.0055
95	4.2038	4.1985			1.00583	1.00479	1.0067
Mean		4.1835					
100							1.0081

Although it is difficult to explain this degree of discord, it seems possible that inaccurate accounting for heat leak may have been responsible for much of the difference. It is difficult to believe that Barnes' estimate in 1909 that the error of the measurements in any part of the range did not exceed 1 part in 10,000, or Callendar's estimate of 1 part in 4,000 for the absolute value of the mechanical equivalent, took into account all the possibilities for deviations from the true values.

Jaeger and von Steinwehr

Their measurements [27] were made at the Physikalisch-Technische Reichsanstalt in 1921, by the electric-heating method, and extending over the range from 5° to 50° C, are free from some of the uncertainties of units and standards which affect much of the earlier work. There is very little doubt that the temperature scale and the electrical standards used were substantially the same as those now in use as international standards. The numerical values as given originally may therefore be taken to represent the experimental data between 5° and 50° C smoothed by an empirical formula of the second degree.

These values are given in table 10 with corresponding NBS values for comparison.

Henning and Jaeger [28] quote the value of 4.1842 int. j/g °C for the heat capacity of water at 15° C., estimating the accuracy as about 2 parts in 10,000. The PTR formula accords with the NBS value at this temperature to this estimated accuracy but, elsewhere, the deviations are larger.

It is of interest to examine the individual experimental results to see to what extent this peculiarity may be the result of the type of formula used. It is a well-known fact that formulas of the power series type often show a pronounced tendency to deviate near the ends of an experimental range, even though fitted to the data by least-squares adjustment.

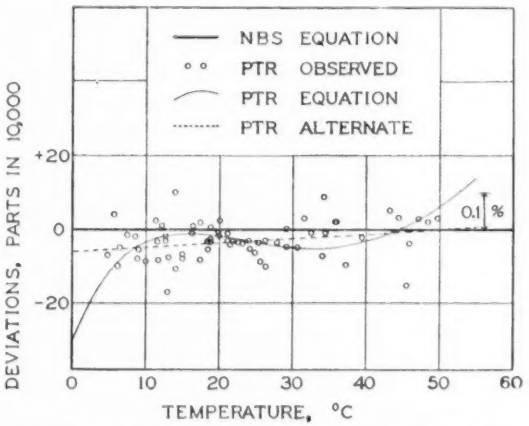

FIGURE 6.—*Deviations of PTR from NBS values of C_p.*

In figure 6 the deviation of the PTR formula from the NBS formula is shown by the smooth curved line. The deviations of the PTR (observed-minus-calculated) values as given by Jaeger and von Steinwehr in their table 11 are shown by the points designated as "PTR obs." The dotted line designated as "PTR Alternate" represents a re-formulation of the PTR data in the light of the present work. This was found by fitting a linear equation to the deviations of the PTR data from the NBS equation, and therefore this alternate interpretation of the PTR results differs from the NBS formulation of C_p only by addition of a correction equal to $[-0.00256+0.0000486t]$. This alternate formulation accords with the observed values slightly better than the PTR equation does, and is of a type which is consistent with experimental data outside their range of temperature. The greater spread of the PTR data is to be expected from the smaller temperature intervals used which were only about 1.4° C, and the general accord may be considered as satisfactory.

TABLE 10.—*Comparison of specific heat values of Jaeger and von Steinwehr with NBS value*

Temperature	Jaeger and von Steinwehr	Jaeger and von Steinwehr alternate	NBS 1939	Temperature	Jaeger and von Steinwehr	Jaeger and von Steinwehr alternate	NBS 1939
°C	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*	°C	*Int. j/g-°C*	*Int. j/g-°C*	*Int. j/g-°C*
5	4.1966	4.1991	4.2014	30	4.1755	4.1766	4.1777
10	4.1897	4.1893	4.1914	35	4.1753	4.1765	4.1774
15	4.1842	4.1832	4.1850	40	4.1764	4.1772	4.1778
20	4.1800	4.1795	4.1811	45	4.1788	4.1783	4.1787
25	4.1771	4.1775	4.1788	50	4.1825	4.1798	4.1799

National Bureau of Standards

The earlier measurements of the enthalpy of saturated water made in this laboratory and published in 1930 [2] furnish data from which values of specific heat of water at 1 atmosphere in the range 0° to 100° C may be derived. These measurements were not intended primarily for determining the specific heat, having been made to furnish data for enthalpy of water and steam for compiling steam tables, and values of the specific heat were not published. Beside other limitations on the accuracy of the NBS 1930 data, the larger temperature intervals then used gave less convincing evidence of the trend of specific heat in the lower range of temperature where the change is most rapid.

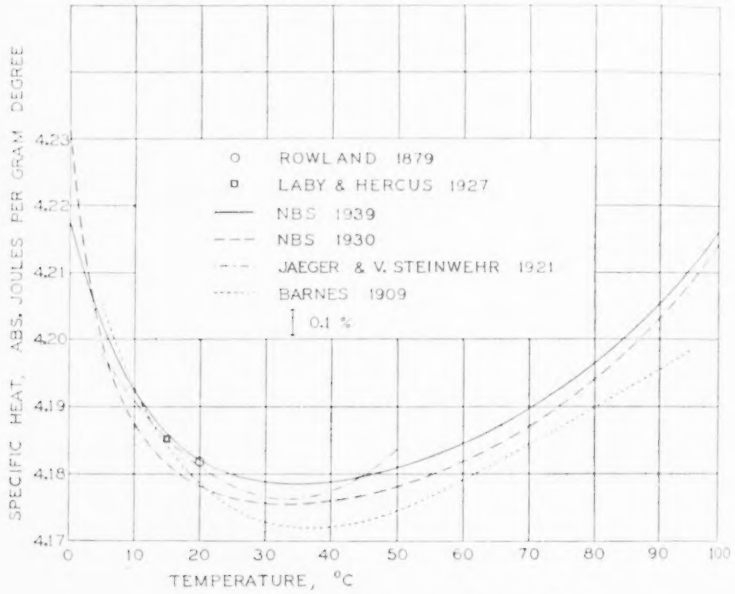

FIGURE 7.—*Comparison of values of* C_p.

Nevertheless, these results have been taken as a basis for values of heat capacity of water used in measurements of enthalpy of superheated steam by several of the laboratories cooperating in the international steam research project. It is therefore of interest to note the difference between the old and the new results, expressed as specific heat. For the purpose of intercomparison, the values of C_p at 1-atmosphere pressure have now been computed from the formulated results of the 1930 report as represented by the following formula given for alpha in the range 0° to 170° C:

$$\alpha = 1.240777 \log_{10}\left(\frac{t+7}{7}\right) + 415.2412\left(\frac{t}{100}\right) + 0.6912\left(\frac{t}{100}\right)^2 - 0.044874\left(\frac{t}{100}\right)^4$$

This computation of C_p was made in a manner similar to those for the present new results as previously described in this report, using the same value for β and $[H_t]^{1\ \mathrm{atm}}_{\mathrm{sat.}}$. The values of C_p thus derived are given in table 11 and are designated as $C_{p\ (\mathrm{NBS\ 1930})}$, together with the 1939 NBS values.

Comparative values of specific heat in absolute joules from the determinations just reviewed are shown graphically in figure 7.

TABLE 11.—*Comparison of specific-heat values of NBS 1930 with NBS 1939 values*

Temperature	C_p NBS 1930	C_p NBS 1939	Temperature	C_p NBS 1930	C_p NBS 1939
°C	*Int. j/g-°C*	*Int. j/g-°C*	°C	*Int. j/g-°C*	*Int. j/g-°C*
0	4.2297	4.2169	50	4.1771	4.1709
5	4.1986	4.2014	55	4.1787	4.1816
10	4.1865	4.1914	60	4.1808	4.1836
15	4.1804	4.1850	65	4.1833	4.1860
20	4.1771	4.1811	70	4.1861	4.1888
25	4.1753	4.1788	75	4.1894	4.1920
30	4.1746	4.1777	80	4.1932	4.1956
35	4.1745	4.1774	85	4.1974	4.1997
40	4.1749	4.1778	90	4.2022	4.2043
45	4.1758	4.1787	95	4.2075	4.2095
			100	4.2134	4.2152

As a summary of the review and comparisons just made, it is found that the results of Rowland, Laby and Hercus, and Jaeger and von Steinwehr for the mechanical or electrical equivalent of the heat capacity of water in the range 15° to 20° C, are corroborated by the results of the present investigation, and are in accord with a value of 1.00019 for the ratio of the international volt-ampere to the absolute, or mechanical watt. It is further found that the results of Jaeger and von Steinwehr throughout their experimental range, 5° to 50° C, are in satisfactory accord with the present NBS results. It has not been found possible to reconcile the discord between the results of Callendar and Barnes and the present NBS results. The likelihood that uncertainty in heat-leak accounting may have been the cause of unsuspected error is suggested. The close control of this factor in the present work may be considered in a choice of definitive values without detracting from esteem of the earlier work.

The values of specific heat derived from the earlier (1930) determinations of the NBS are less trustworthy than the new results and are not considered by the authors as entitled to inclusion in any new appraisal of values of specific heat in the range 0° to 100° C.

Part 3. Heat of Vaporization of Water in the Range 0° to 100° C

I. INTRODUCTION

The heat of vaporization of water is not only a large part of the enthalpy, or heat content, of steam, but it is also one of the terms in the Clapeyron equation by which saturation specific volumes are correlated with saturation vapor pressure. Hence, independent values of this property are important data in the compilation of tables of the properties of steam.

The existing data from direct measurements in the range 0° to 100° C by different experimenters lacked the accord desired in standard steam tables. In the range 0° to 50° C, the deviations of these values from the international skeleton table were as much as 0.2 percent. Since the skeleton table was based on appraisal of the whole ensemble of available data, which in this region were relatively scanty, it was desired to obtain a more positive verification by a systematic redetermination of the heat of vaporization.

This was undertaken in connection with the redetermination of the heat capacity of liquid water from 0° to 100° C, and in the construc-

tion of the calorimeter, as described in part 1, provision was made for measurements of heat of vaporization. Without sacrifice of the aim of high precision in the heat-capacity measurements, it was possible to include features adapting the apparatus to accurate vaporization measurements over the range 0° to 100° C.

II. METHOD AND APPARATUS

Since the method and apparatus have been described in part 1, only a brief resumé is given here of the general scheme of measurement before describing the experimental procedure in detail.

The calorimeter, consisting of a metal shell, protected from unmeasured heat leak by a controlled insulating envelope, contained a sample of air-free water, both liquid and vapor. The liquid was vigorously circulated through an electric heater by an immersed pump.

In the vaporization experiments the measured heat was supplied electrically to evaporate liquid, while vapor was withdrawn at a rate which was controlled manually to keep a constant temperature of evaporation. The energy added per unit mass removed as vapor, designated as gamma, γ, exceeds the latent heat of vaporization, L, by the quantity beta, β. That is, according to the theory [1]

$$\gamma = L + \beta$$

where

$$\beta = T\, u \frac{dP}{dT}$$

The values of β used in deriving values of L from the observed values of γ were calculated from known values of the vapor-pressure derivative, dP/dT, and of u, the specific volume of the liquid. This reduction term is very small at low pressures, and at 100° C amounts to only 1/1600 of γ.

III. EXPERIMENTAL PROCEDURE

1. ACCOUNTING FOR MASS, ENERGY, AND CHANGE IN STATE OF THE WATER SAMPLE

The accounting for the mass, energy, and change in state of the water sample in the vaporization experiments was for the most part the same as in the heat-capacity experiments. The few differences will be pointed out briefly here.

The amount of water evaporated and collected by condensation in an average experiment was about 20 g. To make the weighings with suitable precision, the glass containers holding the condensed water samples were subjected to a standard conditioning treatment before weighing them. The glass container, after a sample of water had been collected as ice by condensation in liquid air, was warmed carefully to melt the ice and bring it slightly above the temperature of the room. The container was then wiped dry and placed in the balance case. Air in the balance case was circulated by a fan for at least 5 min to bring the container to the balance case temperature as well as to insure a standard surface condition. Weighings were then made by substitution, estimating to one-tenth of a milligram. A substitute or tare glass container, which displaced the same amount

of air as the weighing container, was kept in the case and was weighed either just before or after the collecting container. This eliminated errors of weighing due to variation in length of the balance arm or change of weight of the counterpoise.

In the vaporization process, larger temperature gradients were induced in the calorimeter than in the heat-capacity experiments. In order to diminish these gradients, the pump speed was increased to 106 rpm at the expense of a larger pump power. Since the pump power was also less constant than before, determinations of it were made oftener. Several pump-power determinations were made on each day, the experiments being arranged so that pump-power determinations were made usually just before and just after one or two evaporation experiments. By interpolating between pump-power determinations, account was taken of changes in pump power, including that due to changes in liquid level. In all, 131 determinations of pump power were made during the 152 evaporation experiments.

Owing to the greater disturbance of temperature by the evaporation process, the heat-leak accounting was slightly less exact than in the heat-capacity measurements. A small supercorrection, depending on the location of the liquid level, was applied, sometimes amounting to as much as 1 part in 50,000.

During the withdrawal of steam from the calorimeter, the upper tube was tempered by the outgoing steam, so for this period there was no correction for heat leak in the upper tube.

The initial and final temperatures of the water in the calorimeter were observed in the same manner as in the heat-capacity experiments. The temperature of the steam leaving the calorimeter was indicated by the group of four thermoelements, *JT*, representing the average temperature of the upper part of the calorimeter, and the single thermoelements, *J7*, *J6*, and *J5*, representing the temperatures along the upper tube.

A study of the thermoelement indications and their correlation with the observed values of heat of vaporization indicated that the temperature of the upper part of the calorimeter (measured by *JT*) is the best representation of the temperature of the steam withdrawn from the calorimeter and likewise of the temperature of evaporation.

Special details of the experimental procedure will next be described.

2. DESCRIPTION OF VAPORIZATION EXPERIMENTS

In preparation for an experiment, the calorimeter was charged with about 800 g of air-free water in the manner described in part 2. Trials with different charges showed that amounts between about 800 and 500 g gave the most satisfactory operating conditions. The calorimeter temperature was adjusted to the chosen temperature of the experiment by either electric heating, or cooling by the process of withdrawing vapor. During this adjustment of the calorimeter temperature, the throttle valve was heated by its electric heater to maintain it warmer than the calorimeter. The envelope temperature also was maintained above the calorimeter temperature. These precautions opposed condensation of water in the upper tube, which later, by removal, might give erroneous accounting for mass and energy. Consistency of the results with varying rates of withdrawal showed that this danger had been removed.

The temperatures of the envelope and reference block were next brought very slightly above the calorimeter temperature. During this period of adjustment, the circulating pump was started and the space between the calorimeter and envelope was evacuated for the purpose of insulation. A weighed evacuated glass container, *SR*, was connected to the vapor line, as shown in figure 3 in part 1. After evacuation of the line, the glass container was opened to the vapor throttle valve. The apparatus was then ready for the beginning of an experiment.

The equilibrium temperature of the calorimeter and contents was observed. At the start of the heating period, the current from the storage battery was shifted from the substitute resistor to the calorimeter heater by the automatic switch actuated by the time signals. Using the indications of the four thermoelements, *JT*, as guides, the throttle valve was opened and steadily adjusted so as to keep the value of *JT* practically zero. The reference block was kept at a constant temperature, as shown by the resistance thermometer indications. In this way, the temperature of the upper part of the calorimeter, which closely followed the evaporation temperature, was maintained constant at the initial reference block temperature by withdrawing enough steam to balance the energy put into the calorimeter. During this time, the bottom part of the calorimeter, which was in contact with the circulating liquid, became warmer than the top part by the amount of superheating necessary to conduct the heat to the surface for evaporation.

In order to evaluate heat-leak factors and the temperature of the withdrawn steam, the thermoelements on the upper tube, lower tube, calorimeter, and envelope were observed at 1-min. intervals. The readings of the resistance thermometer were recorded every minute so that the thermoelement observations could be referred to the International Temperature Scale. Occasional surveys of all thermoelements were made to guide proper control of the experiments. The current and potential drop in the calorimeter heater were observed on alternate minutes starting ½ minute after the power was switched on. At the end of the chosen number of minutes, the calorimeter heating was stopped and enough more vapor withdrawn before closing the valve to bring the calorimeter and contents to final equilibrium temperature near the initial temperature. The final temperature was then observed.

In all, 152 satisfactory vaporization experiments were made between 0° and 100° C. For most of these experiments, the time of evaporation was about 20 min., and the total time of the experiment about 30 min. Of these, 64 experiments were made at an evaporation rate of about 1 g/min. In tests to detect any significant change of the result with the rate of withdrawal, a number of the other experiments were made at various rates ranging from 0.25 to 2.22 g/min. The purpose of these tests was to ascertain whether there was any appreciable amount of liquid in the steam withdrawn. Examination of the results revealed no definite evidence of such an effect.

IV. RESULTS OF VAPORIZATION EXPERIMENTS

The data and computations for the vaporization experiments were so similar to those described in part 2 for the heat-capacity experiments that sample sheets need not be given. The principal data from the

vaporization experiments, as reduced to give values of gamma, γ, are given in table 12. In addition to the data taken in the heat-capacity experiments, both thermometer readings and the thermoelement, JT, readings were observed every minute during the evaporation period. The combination of the readings permitted the calculation throughout the experiment of the temperature of the top part of the calorimeter, which was found to represent closely the temperature of evaporation.

The computations of temperature and electric energy were made in the same manner as in the heat-capacity computations. In computing the total energy, the corrections were made as shown previously, except that in the case of the upper tube the heat leak was considered as zero during the outflow of steam. A correction was always necessary to account for the energy involved in the difference of the final temperature of the calorimeter and contents from the initial temperature. This correction was usually for temperature changes of less than 0.01°C, and was calculated, using the data from the heat-capacity experiments. Values are given in table 12 as "corrections for change of temperature."

Dividing the total energy thus obtained by the mass of water withdrawn gives a value of gamma, γ, at the effective evaporation temperature. This temperature was usually within 0.03° C of the even temperature, making the correction applied to the energy for the difference usually less than 1 part in 30,000.

The mean values of γ at the even temperatures were then found, weighting the separate determinations in proportion to the rates of evaporation. These weighted means and the deviations of the measured values from them are given in table 12. Study of the deviations justifies this mode of weighting for the rates used. The results were then ready for final formulation for use in computing heat of vaporization.

TABLE 12.—*Principal data from vaporization experiments*

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at even temperature	Deviation from weighted mean
	°C	*g/min*	*g*	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Int. j/g*	*Int. j/g*
5-5-38	0.13	0.63	12.6135	−1.9	33.3	−12.7	31,539.0	2500.73	0.01
5-5-38	.15	.63	12.6135	−2.3	31.8	−7.0	31,542.1	2501.01	.29
5-5-38	.15	.63	12.6076	−1.9	32.4	−33.0	31,522.9	2500.67	−.06
5-5-38	.16	.63	12.6365	−3.9	32.9	44.5	31,592.6	2500.49	−.23
5-5-38	.14	.63	12.6160	−2.0	33.5	−5.2	31,544.6	2500.69	−.03
Even temperature 0.0° C. Weighted mean value of $\gamma_{0.0}$=2500.72 int. j/g.									
3-14-38	1.12	0.28	5.5299	−1.9	20.6	19.7	13,810.9	2497.78	−0.14
3-14-38	1.12	.65	12.9825	−3.6	21.3	1.4	32,419.9	2497.48	−.44
3-15-38	1.09	.70	14.0974	−2.3	32.2	−2.4	35,212.4	2498.00	.08
3-15-38	1.11	.70	14.0984	−3.5	23.6	4.7	35,209.4	2497.66	−.26
3-30-38	1.03	.70	14.0606	−2.0	27.0	17.9	35,118.8	2497.74	−.18
3-30-38	1.02	.70	14.0586	−2.2	26.1	22.6	35,115.0	2497.81	−.11
3-30-38	1.03	.25	4.9895	−.2	25.5	−18.5	12,464.2	2498.15	.23
3-30-38	1.03	.25	5.0069	−.2	24.4	−2.5	12,488.1	2497.24	−.68
3-30-38	1.02	.25	5.0032	−.2	25.3	7.2	12,495.7	2497.59	−.33
3-30-38	1.03	.25	4.9988	−.5	25.7	−2.7	12,484.0	2497.47	−.45
5-4-38	0.99	.70	14.0962	−1.4	25.5	9.2	35,215.8	2498.23	.31
5-4-38	1.00	.71	14.1013	−1.5	26.1	9.9	35,228.3	2498.23	.31
5-4-38	1.00	.70	14.0920	−1.4	28.3	−12.8	35,205.0	2498.23	.31
5-4-38	1.00	.71	14.1014	−1.4	27.1	1.2	35,227.7	2498.18	.26
5-4-38	1.00	.71	14.1054	−1.3	27.6	6.8	35,236.7	2498.10	.18
Even temperature 1.0° C. Weighted mean value of $\gamma_{1.0}$=2497.92 int. j/g.									

TABLE 12.—*Principal data from vaporization experiments*—Continued

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at even temperature	Deviation from weighted mean
	°C	g/min	g	Int. j	Int. j	Int. j	Int. j	Int. j/g	Int. j/g
3-31-38	5.00	0.91	18.1421	−2.6	28.7	26.7	45,142.0	2488.24	−0.10
3-31-38	5.00	.91	18.1191	−3.9	29.2	−11.8	45,089.1	2488.48	.14
3-31-38	5.01	.25	5.0913	−.8	29.6	−3.4	12,669.4	2488.46	.12
3-31-38	5.02	.25	5.0952	−.9	29.5	−13.3	12,677.7	2488.22	−.12
5-3-38	5.02	.25	5.0972	−1.1	29.3	−5.8	12,683.7	2488.32	−.02
5-3-38	5.00	.92	18.3058	−8.7	24.4	−12.4	45,553.6	2488.48	.14
5-3-38	5.00	.92	18.3167	−5.5	23.0	−15.1	45,579.2	2488.39	.05
5-3-38	5.00	.92	18.3298	−4.5	23.1	3.2	45,609.4	2488.27	−.07
5-3-38	5.00	.92	18.3372	−4.0	23.1	4.7	45,627.5	2488.25	−.09
5-3-38	5.01	.92	18.3425	−2.7	23.2	−1.9	45,639.9	2488.22	−.12
5-3-38	5.01	.92	18.3463	−2.2	23.3	2.3	45,651.5	2488.35	.01

Even temperature 5° C. Weighted mean value of γ_5=2488.34 int. j/g.

3-22-38	10.04	0.56	11.2389	−5.6	27.3	−7.0	27,836.6	2476.90	0.17
3-22-38	10.05	.26	5.1646	−2.4	28.4	−8.8	12,788.6	2476.32	−.41
3-22-38	10.07	1.05	20.9428	−9.8	30.4	−12.1	51,862.3	2476.54	−.19
4-1-38	9.97	1.03	10.3408	−2.9	19.4	−9.9	25,609.1	2476.44	−.29
4-1-38	9.99	0.26	5.1040	−0.9	30.0	−2.6	12,640.0	2476.47	−.26
4-1-38	9.99	.26	5.1106	−.8	31.0	−0.7	12,659.3	2477.05	.32
4-1-38	10.01	.26	5.1326	−.9	31.5	7.4	12,711.9	2476.74	.01
4-1-38	10.01	.26	5.1070	−.8	31.5	−13.8	12,647.6	2476.54	−.19
4-1-38	10.01	.26	5.1057	−.9	31.5	−16.6	12,643.2	2476.31	−.42
4-25-38	10.00	1.03	20.5761	−6.7	24.5	27.5	50,971.4	2477.21	.48
4-25-38	10.01	1.03	20.5738	−6.3	21.9	−25.6	50,953.8	2476.65	−.08
4-25-38	10.02	0.57	11.3193	−2.4	26.0	−1.0	28,019.9	2477.14	.41
4-25-38	10.02	.57	11.3326	−2.1	27.3	8.4	28,037.4	2477.00	.27
4-25-38	10.03	.57	18.5282	−4.0	28.2	8.4	28,065.2	2476.55	−.18

Even temperature 10° C. Weighted mean value of γ_{10}=2476.73 int. j/g.

3-28-38	15.04	1.04	20.8145	−13.2	27.4	5.6	51,306.7	2465.04	0.23
3-28-38	15.04	1.04	20.7958	−10.4	27.3	−7.4	51,255.2	2464.78	−.03
3-28-38	15.06	0.26	5.1292	−2.3	27.9	−3.9	12,642.1	2464.87	.06
3-28-38	15.06	.26	5.1420	−2.5	30.4	5.9	12,674.7	2465.08	.27
3-28-38	15.06	.26	5.1417	−2.6	28.9	−0.2	12,671.8	2464.66	−.15
3-28-38	15.06	.26	5.1421	−2.6	29.3	−3.7	12,669.3	2463.98	−.83

Even temperature 15° C. Weighted mean value of γ_{15}=2464.81 int. j/g.

3-21-38	20.05	0.57	11.3473	−6.9	28.7	−12.4	27,841.8	2453.73	0.37
3-21-38	20.06	.57	11.3539	−6.4	28.3	2.3	27,860.8	2453.99	.63
3-21-38	20.08	.26	5.2151	−2.6	27.7	−10.8	12,797.3	2454.08	.72
4-26-38	20.10	1.06	16.9431	−9.8	23.0	1.9	41,561.4	2453.24	−.12
4-26-38	19.98	1.03	20.6986	−6.5	25.2	−20.2	50,779.4	2453.22	−.14
4-26-38	19.99	1.03	20.6905	−6.8	27.5	−20.1	50,758.2	2453.19	−.17
4-26-38	20.01	0.57	11.3518	−3.0	26.1	−4.8	27,849.1	2453.30	−.06
4-26-38	20.02	.57	11.3453	−3.1	26.3	−22.2	27,835.7	2453.55	.19
4-26-38	20.02	.57	11.3570	−3.2	26.5	1.4	27,856.5	2452.85	−.51
4-26-38	20.03	.57	11.3506	−3.3	27.7	2.0	27,845.5	2453.15	−.21

Even temperature 20° C. Weighted mean value of γ_{20}=2453.36 int. j/g.

3-25-38	25.01	1.06	21.1489	−8.8	26.3	1.3	51,627.7	2441.17	−0.14
3-25-38	25.01	1.06	21.1399	−7.8	26.2	−.5	51,610.4	2441.39	.08
3-25-38	25.01	.26	5.2053	−1.6	26.1	−11.9	12,706.7	2441.13	−.18
3-25-38	25.03	.26	5.2216	−2.0	26.8	5.2	12,744.0	2440.70	−.61
3-25-38	25.03	.26	5.2151	−1.9	25.5	−11.4	12,726.1	2440.31	−1.00
4-4-38	24.99	.29	5.7987	−1.3	23.7	−44.6	14,160.0	2441.91	.60
4-4-38	24.99	.57	11.4234	−3.9	24.7	−18.9	27,893.9	2441.80	.49
4-4-38	25.00	1.05	21.1590	−5.2	28.0	−19.9	51,652.3	2441.21	−.10
4-4-38	25.01	1.05	20.9658	−4.6	15.6	28.6	51,188.2	2441.53	.22
4-8-38	24.98	1.05	21.2868	−13.6	24.5	23.2	51,952.5	2440.55	−.76
4-8-38	24.98	2.08	41.5416	−21.0	26.6	−40.3	101,426.3	2441.51	.20
4-8-38	25.01	.29	5.7624	−2.3	25.7	−12.0	14,071.6	2441.99	.68
4-8-38	25.01	.57	11.3594	−6.3	23.5	.3	27,735.8	2441.68	.37

Even temperature 25° C. Weighted mean value of γ_{25}=2441.31 int. j/g.

TABLE 12.—*Principal data from vaporization experiments*—Continued

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at even temperature	Deviation from weighted mean
	°C	g/min	g	Int. j	Int. j	Int. j	Int. j	Int. j/g	Int. j/g
3-19-38	30.02	0.57	11.4735	−6.4	25.1	−17.8	27,880.5	2430.04	0.61
3-19-38	30.03	.57	11.4791	−6.6	25.8	−7.4	27,893.3	2429.99	.56
4-12-38	30.03	2.15	42.9434	−11.9	25.9	−11.5	104,302.5	2428.91	−.52
4-12-38	30.04	2.15	42.9255	−12.0	23.9	−31.3	104,266.4	2429.12	−.31
4-13-38	30.00	.29	5.8389	−2.4	26.9	−5.0	14,185.1	2429.41	−.02
4-13-38	30.01	.29	5.8419	−2.5	26.9	5.2	14,194.9	2429.86	.43
4-13-38	30.01	.58	11.5218	−5.7	26.9	1.1	27,990.2	2429.34	−.09
4-13-38	30.01	.58	11.5076	−5.1	27.0	−11.2	27,959.8	2429.70	.27
4-13-38	30.01	1.07	21.4137	−10.7	27.7	−1.3	52,032.2	2429.88	.45
4-13-38	30.01	1.07	21.4173	−10.4	29.3	.2	52,037.6	2429.72	.29
4-13-38	30.01	1.07	21.4198	−10.1	30.7	3.6	52,041.0	2429.57	.14
	Even temperature 30° C. Weighted mean value of γ_{30}=2429.43 int. j/g.								
3-18-38	40.03	0.58	11.6219	−6.2	24.3	9.3	27,962.7	2406.10	0.23
3-18-38	40.04	.58	11.6027	−5.9	25.5	−5.7	27,918.9	2406.34	.47
3-18-38	40.05	1.08	21.6436	−13.9	26.1	25.7	52,067.5	2405.82	−.05
3-18-38	40.05	.27	10.6672	−5.9	44.1	−2.5	25,664.4	2406.04	.17
4-18-38	40.02	.29	5.8071	−3.6	24.7	−3.7	13,971.8	2406.04	.17
4-18-38	40.02	.29	5.8067	−3.4	29.1	−9.8	13,988.9	2405.70	−.17
4-18-38	40.02	.58	11.5896	−7.6	25.1	8.5	27,883.7	2405.97	.10
4-18-38	40.02	1.10	22.0565	−14.6	25.5	1.3	53,065.9	2405.96	.09
4-18-38	40.03	2.10	42.0339	−26.8	26.8	5.8	101,117.2	2405.68	−.19
4-18-38	40.03	2.10	42.0039	−24.3	29.1	−9.2	101,049.1	2405.78	−.09
	Even temperature 40° C. Weighted mean value of γ_{40}=2405.87 int. j/g.								
3-17-38	50.03	0.58	11.7417	−9.1	21.2	−4.2	27,971.7	2382.32	0.48
3-17-38	50.04	.58	11.7431	−8.7	23.4	0.3	27,975.5	2382.39	.55
3-17-38	50.05	.30	5.9655	−2.9	25.0	−26.5	14,211.8	2382.45	.61
4-15-38	50.03	2.13	42.6496	−16.8	18.9	−25.6	101,565.8	2381.47	−.37
4-15-38	50.04	0.30	6.0205	−2.0	18.6	8.6	14,336.3	2381.35	−.49
4-15-38	50.04	.30	6.0117	−2.3	20.0	−16.8	14,318.2	2381.82	−.02
4-15-38	50.04	.58	11.7121	−4.8	20.9	−1.9	27,894.8	2381.81	−.03
4-15-38	50.04	.58	11.7095	−4.8	21.4	−7.5	27,885.6	2381.55	−.29
4-15-38	50.05	1.09	21.8394	−7.4	22.8	−31.8	52,017.0	2381.92	.08
5-25-38	49.99	1.08	21.5345	−4.4	27.3	17.8	51,292.4	2381.85	.01
5-25-38	49.99	1.08	21.5660	−5.4	28.8	17.4	51,372.4	2382.08	.24
	Even temperature 50° C. Weighted mean value of γ_{50}=2381.84 int. j/g.								
5-13-38	59.99	1.12	22.4288	−22.0	25.5	−10.7	52,891.7	2358.18	0.53
5-13-38	59.99	1.12	22.4230	−19.5	24.7	−21.0	52,870.3	2357.84	.19
5-13-38	60.01	2.20	44.0762	−29.6	29.9	−9.7	103,905.8	2357.43	−.22
5-13-38	60.00	2.20	44.0688	−24.2	27.3	14.0	103,889.5	2357.44	−.21
5-13-38	60.01	1.12	22.4740	−10.7	32.4	−7.7	52,983.3	2357.56	−.09
5-13-38	60.02	1.12	17.9796	−8.4	25.7	−2.1	42,392.7	2357.87	.22
5-25-38	60.01	1.09	21.7726	−8.9	26.5	−10.6	51,333.5	2357.73	.08
5-25-38	60.01	1.09	21.7708	−8.4	26.7	75.7	51,325.9	2357.58	−.07
	Even temperature 60° C. Weighted mean value of γ_{60}=2357.65 int. j/g.								
5-9-38	70.01	2.18	21.7659	−14.3	16.7	−46.9	50,787.9	2333.39	0.14
5-9-38	70.02	1.12	22.4433	−19.1	25.7	34.5	52,366.3	2333.32	.07
5-9-38	70.02	1.12	22.4376	−18.0	22.5	−8.5	52,352.2	2333.29	.04
5-9-38	70.01	1.12	22.4550	−17.7	22.5	21.7	52,386.9	2332.99	−.26
5-9-38	70.02	1.12	22.4530	−14.7	23.3	1.9	52,381.7	2333.00	−.25
5-9-38	70.02	1.12	22.4598	−13.3	25.2	23.7	52,406.1	2333.38	.13
	Even temperature 70° C. Weighted mean value of γ_{70}=2333.25 int. j/g.								
5-24-38	80.06	1.10	11.0280	−4.3	19.8	−28.7	25,456.1	2308.47	−0.04
5-24-38	80.08	1.10	22.0315	−15.3	25.5	−17.6	50,856.3	2308.54	.03
5-24-38	80.08	1.11	22.2351	−15.6	29.9	−0.1	51,329.2	2308.68	.17
5-24-38	80.09	1.11	22.2461	−12.3	28.8	9.9	51,349.2	2308.45	−.06
5-24-38	80.08	1.11	23.4033	−11.2	28.9	69.8	54,019.6	2308.40	−.11
5-26-38	80.00	1.10	22.0608	−12.3	38.3	−4.0	50,932.6	2308.74	.23
5-26-38	80.00	1.10	22.0742	−12.2	39.1	20.6	50,959.5	2308.55	.04
5-26-38	80.01	0.63	12.5791	−5.8	39.1	8.2	29,040.1	2308.62	.11
5-26-38	80.01	.63	12.5686	−6.2	38.7	−10.1	29,014.5	2308.51	.00
5-26-38	80.03	.63	12.5666	−6.5	38.2	2.4	29,007.1	2308.34	−.17
5-26-38	80.03	.63	12.5659	−6.5	38.0	5.0	29,002.5	2308.10	−.41
	Even temperature 80° C. Weighted mean value of γ_{80}=2308.51 int. j/g.								

TABLE 12.—*Principal data from vaporization experiments*—Continued

Date	Evaporation temperature	Approximate rate	Mass of vapor removed	Heat leak	Pump energy	Correction for change in temperature	Entire energy added	γ at even temperature	Deviation from weighted mean
	°C	g/min	g	Int. j	Int. j	Int. j	Int. j	Int. j/g	Int. j/g
5-10-38	90.01	2.22	22.1958	−9.4	18.4	−2.8	50,683.1	2283.48	0.07
5-10-38	90.01	2.22	44.3722	−22.9	31.8	8.7	101,321.2	2283.47	.06
5-10-38	90.01	1.16	23.2875	−13.9	36.1	−8.9	53,171.6	2283.30	−.11
5-10-38	90.01	1.17	23.3241	−12.0	38.9	3.9	53,255.2	2283.30	−.11
Even temperature 90° C. Weighted mean value of γ_{90}=2283.41 int. j/g.									
5-11-38	99.99	1.18	23.5914	−13.7	33.9	4.3	53,261.8	2257.65	0.23
5-11-38	100.00	1.18	23.5977	−13.7	31.8	3.4	53,272.1	2257.51	.10
5-11-38	100.01	0.63	12.5763	−7.8	31.8	−7.0	28,392.8	2257.66	.34
5-11-38	100.01	.63	12.5796	−8.0	30.9	−4.2	28,396.0	2257.33	.01
5-11-38	100.01	.63	12.5795	−8.1	31.1	−6.7	28,393.3	2257.13	−.19
6-1-38	99.99	1.13	22.5785	−25.6	24.9	53.0	50,964.4	2257.18	−.14
6-1-38	99.99	1.13	22.5522	−24.8	21.5	−6.5	50,900.1	2256.96	−.36
6-1-38	99.99	1.13	22.5650	−18.4	21.4	17.4	50,932.4	2257.11	−.21
6-1-38	99.99	1.13	22.5745	−14.3	18.9	19.3	50,946.0	2256.76	−.56
6-2-38	100.00	1.12	22.4874	−14.3	28.0	−12.2	50,766.3	2257.54	.22
6-2-38	100.01	1.12	22.4909	−13.8	24.6	3.2	50,778.9	2257.78	.46
6-2-38	100.01	1.12	22.4899	−12.6	24.1	−2.6	50,764.6	2257.25	−.07
6-2-38	100.01	1.12	22.4959	−11.7	23.6	3.3	50,776.8	2257.19	−.13
6-3-38	100.01	1.13	22.5822	−11.2	29.2	29.0	50,977.9	2257.47	.15
6-3-38	100.01	1.13	22.5659	−10.9	29.9	1.2	50,939.2	2257.38	.06
6-3-38	100.02	1.13	22.5644	−10.2	30.2	3.1	50,931.4	2257.21	−.11
6-3-38	100.02	1.13	22.5616	−10.8	30.3	9.4	50,927.8	2257.33	.01
Even temperature 100° C. Weighted mean value of γ_{100}=2257.32 int. j/g.									

In addition to the measurements described here, there was a series of results of similar measurements made in this laboratory (1930–32) [2, 29] with an earlier stirred calorimeter and extending from 50° to 270° C; also another series (1937) [3] extending from 100° to 374° C, made with a later unstirred calorimeter.

Although these older measurements lacked some of the refinements of the present series, the fact that they were obtained with two calorimeters of different design from the present calorimeter and covered a much greater range of temperature, entitles them to inclusion in the scheme of formulation. In the range where they overlap or duplicate present measurements, the degree of accord furnishes a measure of the corroboration, while the greater range of the older data contributes greater directive control to a formulation than would result from the more accurate present results. A formulation was sought which comprised a smoothed appraisal of the experimental evidence over considerable range, and an empirical equation for γ was derived which satisfactorily does this over the range 0° to 200° C. After appraising the reliability of the various measurements, it was decided to weight them according to the number of observations and to give the observations of 1930–32 and those of 1937, respectively, one-fourth and one-half the weight of the observations of the present series.

The empirical equation for γ, as finally adjusted to these weighted data by the least-squares method, is written

$$\gamma = 2500.5 - 2.3233t - 10^x,$$

where $x + 5.1463 - 1{,}540/T$, t is in degrees centigrade, T is in degrees Kelvin (t+273.16), and γ is in international joules per gram. This equation represents not only the present values of γ between 0° and

100° C but also the earlier values between 50° and 200° C from previous reports. The degree of accord between the observed and calculated values is shown graphically in figure 8.

Between 170° and 200° C the equation gives values which are practically identical with the formulation of 1937, and therefore these values merge smoothly in this region. From 0° to 200° the new formulation supersedes the previous one, and together they complete the determination of γ over the entire range from the ice point to the critical region.

Values of the latent heat of vaporization, L, are calculated from γ by applying the corresponding values of β, which are computed as described in part 2 of this report. Table 13 includes the experimental mean values of γ which were used in the formulation, corresponding values of β, and calculated values of γ and L.

Values of the specific volume of the saturated vapor, u', were calculated from γ by the relation

$$\gamma = u' TdP/dT.$$

The values of the Clapeyron factor, TdP/dT, were calculated from vapor-pressure derivatives, as described in part 2.

TABLE 13.—*Formulation of data on heat of vaporization*

Temperature	γ, Observed				γ, calculated	β	Heat of vaporization, L	Clapeyron factor $T\frac{dP}{dT}$	Specific volume of vapor v'
	1930, 1932.	1937	1939	Weighted mean					
°C	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/dm³*	*cm³/g*
0			2500. 72	2500. 72	2500. 18	0. 012	2500. 17	12. 1198	206288
1			2497. 92	2497. 92	2497. 84				
5			2488. 34	2488. 34	2488. 48	. 017	2488. 46	16. 9112	147150
10			2476. 73	2476. 73	2476. 76	. 023	2476. 74	23. 2730	106422
15			2464. 81	2464. 81	2465. 02	. 032	2464. 99	31. 6138	77973
20			2453. 36	2453. 36	2453. 25	. 042	2453. 21	42. 4173	57836
25			2441. 31	2441. 31	2441. 46	. 056	2441. 40	56. 2535	43401
30			2429. 43	2429. 43	2429. 64	. 074	2429. 57	73. 7846	32929
35					2417. 78	. 096	2417. 68	95. 7734	25245
40			2405. 87	2405. 87	2405. 88	. 124	2405. 76	123. 089	19546
45					2393. 93	. 158	2393. 77	156. 714	15275
50	2382. 0		2381. 84	2381. 85	2381. 93	. 200	2381. 73	197. 752	12045
55					2369. 88	. 251	2369. 63	247. 430	9578. 0
60			2357. 65	2357. 65	2357. 76	. 312	2357. 45	307. 097	7677. 6
65					2345. 58	. 386	2345. 19	378. 234	6201. 4
70	2333. 9		2333. 25	2333. 40	2333. 31	. 473	2332. 84	462. 470	5045. 3
75					2320. 97	. 576	2320. 39	561. 544	4133. 2
80			2308. 51	2308. 51	2308. 53	. 697	2307. 83	677. 319	3408. 3
85					2296. 00	. 838	2295. 16	811. 815	2828. 2
90	2283. 7		2283. 41	2283. 45	2283. 35	1. 001	2282. 35	967. 152	2360. 9
95					2270. 60	1. 191	2269. 41	1145. 57	1982. 1
100	2258. 71	2257. 79	2257. 32	2257. 73	2257. 71	1. 408	2256. 30	1349. 52	1673. 0
130	2177. 15			2177. 15	2177. 26				
150	2119. 64	2119. 50		2119. 57	2119. 87				
170	2058. 78			2058. 78	2058. 63				
200	1957. 96	1957. 11		1957. 44	1957. 93				

V. COMPARISONS WITH EARLIER WORK

A review of determinations of heats of vaporization of water previous to 1930 has already been made by Fiock [24]. No further attempt will be made here to review critically those determinations. However, since some of the results of earlier experiments are expressed in terms of the heat capacity of water, it is necessary to use heat-capacity data to convert those results to electric-energy units. In the review by Fiock these conversion data were obtained from the 1930 measurements at the NBS. The measurements given in part 2 of this report supply more accurate conversion data which will be used, where necessary, to interpret early results. The determinations of heats of vaporization will be briefly mentioned.

Dieterici

Dieterici [30] used a Bunsen ice calorimeter to measure the heat of vaporization at 0° C. In interpreting his results, uncertainty in units is avoided by using his own calibration of his ice calorimeter in terms of the mean calorie. By using the NBS value of the mean calorie along the saturated path (4.1903 int. j/g-°C) Dieterici's value of the heat of vaporization at 0° C becomes 2492.2 int. j/g.

Griffiths

Griffiths [31] measured the heats of vaporization at 30° and 40° C. The greatest uncertainty in the reduction of his data is in the evaluation of his electrical units. On the assumption that the electromotive force of his Clark cell was 1.4328 int. v instead of the 1.4342 that he used, his values are

$L_{30°} = 2425.2$ int. j/g $\qquad$ $L_{40°} = 2400.0$ int. j/g

Henning

Henning [32] made measurements in 1906 on the heat of vaporization between 30° and 100° C. His summary in 1919 gives values of his formulated results below 100° C, as follows:

$L_{30°} = 2426.0$ int. j/g.
$L_{40°} = 2403.8$ int. j/g.
$L_{50°} = 2380.8$ int. j/g.
$L_{60°} = 2357.4$ int. j/g.
$L_{70°} = 2333.1$ int. j/g.
$L_{80°} = 2308.0$ int. j/g.
$L_{90°} = 2282.5$ int. j/g.
$L_{100°} = 2255.7$ int. j/g.

A. W. Smith

Smith [33] made determinations between 14° and 100° C by evaporating water into a stream of air. Correction is made to the 1907 data for the revised Clark cell voltage. The values from Smith's experiments are as follows:

$L_{14°} = 2463.5$ int. j/g.
$L_{21°} = 2447.6$ int. j/g.
$L_{28°} = 2431.1$ int. j/g.
$L_{40°} = 2401.4$ int. j/g.
$L_{100°} = 2261.6$ int. j/g.

Richards and Mathews

Richards and Mathews, and Mathews [34] measured the heat of vaporization at 100° C by a condensation method. After correction of the 1911 series, as later suggested by Mathews, the 1911 and 1917

series yield essentially the same result. Using the 1939 NBS heat-capacity data, their average value for the heat of vaporization at 100° C is 2257.3 int. j/g.

Carlton-Sutton

Carlton-Sutton [35] used a modification of Joly's classical apparatus to measure the heat of condensation of water directly in terms of the mean calorie without any reference to electrical standards. His final value of 538.88 mean cal, when interpreted by the NBS–39 value for

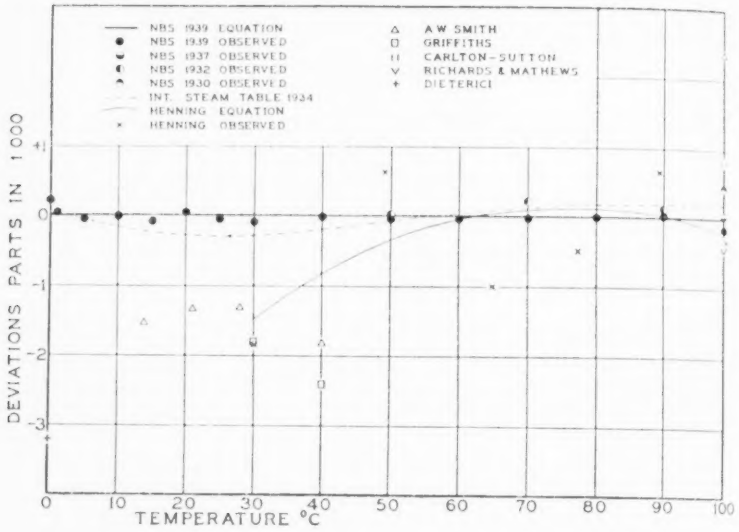

FIGURE 8.—*Comparison of values of heat of vaporization.*

the mean calorie along the saturated path, yields the value 2258.0 int. j/g for the heat of vaporization at 100° C.

National Bureau of Standards

Measurements at the National Bureau of Standards in 1930 [2] and 1932 [29] were made with an earlier calorimeter of different design from that of the present calorimeter. The observed values of heat of vaporization, L, in the range 50° to 100° C were:

$L_{50}° = 2381.8$ int. j/g. $L_{90}° = 2282.7$ int. j/g.
$L_{70}° = 2333.6$ int. j/g. $L_{100}° = 2257.3$ int. j/g.

Measurements above 100° C were made at the National Bureau of Standards in 1937 [3] with another calorimeter. The value observed in 1937 of heat of vaporization, L, at 100° C, was 2256.38 int. j/g.

It is believed that the measurements made with these two earlier calorimeters are inferior in precision to the present results using an improved calorimeter, but since these earlier results were obtained in calorimeters of different design from that of the present, they were included in the formulation in the present report.

In figure 8, a comparison is given of the various measurements of the heats of vaporization between 0° and 100° C. The base line in this figure is taken from the NBS–39 formulation.

The formulations of heat capacity and heat of vaporization, which have been given in this report, are considered more reliable than those given in previous reports from this laboratory in the range 0° to 100° C. Inasmuch as the values of some of the properties of saturated water and steam above 100° C depend partly on the values below 100° C a reappraisal has been made of all the measurements made at the National Bureau of Standards and the results compiled into a single table of smoothed values in the entire range 0° to 374.15° C. This compilation appears elsewhere in this journal [36].

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THERMAL PROPERTIES OF SATURATED WATER AND STEAM

By Nathan S. Osborne, Harold F. Stimson, and Defoe C. Ginnings

ABSTRACT

The completion of new measurements of heat capacity and heat of vaporization of water in the range 0° to 100° C has contributed new data which affect the accepted values of the saturation properties of water and steam in the whole range up to the critical region. With these new data, it is now possible to compile the results of the entire series of measurements which have been carried out in this laboratory into a single table of smoothed values of the properties of saturated water and steam. The compilation presented supersedes the previous tabulations which have accompanied reports of the experimental measurements in this laboratory.

The properties of saturated steam and water included in the tables presented in this compilation are vapor pressure, specific volume, enthalpy, and entropy.

In the previous reports [1, 2, 3, 4][1], data obtained by calorimetric measurements have been given in several partial contributions, none of which has covered the entire range 0° to 374° C. It is the purpose of the present compilation to assemble these data into a thermodynamically consistent group, with the experimental irregularities smoothed out by the use of formulations. As far as possible, the formulas used, both empirical and theoretical, are indicated, and the experimental bases of the empirical formulas are also given. The units used are the same as those in the International Steam Tables [9].

It will be convenient to give the descriptions in two main parts, the first being for the range 0° to 100° C and the second from 100° to 374.15° C, since most of the reductions in the range 0° to 100° C have already been made in the report [4] on the experimental work, which is being published at this time. In that report an account is given of the measurements of the heat capacity and heat of vaporization of water, including the reduction of the data to give values of specific heat, enthalpy of both liquid and vapor, and specific volume of the vapor. The values in this range are taken directly from the report, making conversions to the units used in this tabulation.

[1] Figures in brackets indicate the literature references at the end of this paper.

From the theory [5] of calorimetry of a saturated fluid, the following relations are obtained, by which enthalpy, entropy, and specific volume are obtained from the calorimetric data.

$$H]_0^t=\alpha]_0^t+\beta]_0^t$$

$$H']_0^t=H]_0^t+L_t$$

$$\Phi]_0^t=\int_0^t\frac{1}{T}\frac{d\alpha dt}{dt}+\left[\frac{\beta}{T}\right]_0^t$$

$$\Phi']_0^t=\Phi]_0^t+\frac{L}{T}$$

$$\beta=uTdP/dt$$

$$\gamma=u'TdP/dt$$

In the above equations H and H' denote enthalpy; Φ and Φ' denote entropy; u and u' denote specific volume, in each case, respectively, of liquid and vapor; L denotes heat of vaporization $(H'-H)$; t is expressed in degrees centigrade, and T in degrees Kelvin $(t+273.16\ °C)$.

In order to calculate the values for entropy, $\Phi]'_0$, from the relation given above, the empirical equation for $d\alpha/dt$ from the previous report [4] is used. This equation is

$$\frac{d\alpha}{dt}=4.1699+15.27t\ (10)^{-6}+0.0467\ (10)^{-0.036t},$$

where $d\alpha/dt$ is given in int.j/g-$°C$. After dividing the right member of this equation by T, the first two terms may be integrated directly in the evaluation of entropy. The third term could then have been integrated by numerical summation, but it was preferred to substitute for it a new empirical function which could be integrated directly. The integral $\{-1964.6\ (10)^{-(6+0.03755t)}\}$ of this new function was substituted for the term $\{0.0467\int_0^t\frac{1}{T}(10)^{-0.036t}\,dt\}$, and this was found to be equivalent to it well within the present requirements. By combining the calculated integrals of the three terms with the corresponding values of β/T, the values of $\Phi]_0^t$ were found for each of the 5° points from 0° to 100° C. By adding the corresponding values of L/T, the values of $\Phi']_0^t$ were found for the entropy of saturated vapor. These were converted to International Steam Table Calories per gram-degree centigrade for inclusion in table 2.

The values for specific volume of saturated liquid (0° to 100° C), given in table 2, were derived from the data of Chappuis [6], Thiessen [7], and Smith and Keyes [8], and are in agreement with the values adopted by the 1934 International Conference on Steam Tables [9].

The values of vapor pressure from 0° to 90° C, inclusive, given in table 2 were obtained by use of an unpublished formulation of the vapor-pressure data of the Reichsanstalt as reformulated by Harold T. Gerry and used by the International Steam Table Conference [9]

as a basis for definitive values. Dr. Gerry has very kindly given permission to quote the empirical equation

$$\log_{10}P=-3.142305\left\{\frac{10^3}{T}-\frac{10^3}{373.16}\right\}+8.2\log_{10}\left(\frac{373.16}{T}\right)$$
$$-0.0024804(373.16-T)$$

in which P is in standard atmospheres and T is in degrees Kelvin. These values of P were converted into kilograms per square centimeter by using the factor 1.033228.

For the remaining portion of the table, 100° to 374.15° C, part of the calorimetric data from previous reports has been reformulated in order to make allowance for the small changes in values below 100° C shown by the latest results.

The enthalpy of saturated liquid was calculated, using the new formula for the α function in the range 100° to 374.15° C, as follows:

$$\alpha_0^t=0.48558+4.17144t-\{0.6058(t-130)^{3.1}-0.01812(t-200)^{3.64}\}10^{-6}$$

This equation gives values of α in international joules per gram. The values merge smoothly with the later more accurate experimental values, immediately below 100° C and are considered to be a good representation of the calorimetric data.

The values of the specific volume of saturated liquid, u, given in table 2, and used for computation of β from 100° to 325 °C, were obtained from the results of Smith and Keyes [8]. From 330 to 374.15° C, the values of β and corresponding values of u were obtained from the calorimetric data of the previous report [3]. The values of P and dP/dt in the range 95° to 374.15° C are from the formula of Osborne and Meyers [10], based on recent measurements.

The values of γ in the range 100° to 190° C were obtained by computation, using the formula given in a recent report [2]

$$\gamma=2500.5-2.3233\ t-10^x,$$

where $x=5.1463-1540/T$, t is in degrees centigrade, T in degrees Kelvin, and γ in international joules per gram. This formula represents an adjusted appraisal of all the measurements of heat of vaporization made in this laboratory in the range 0° to 220° C and merges smoothly with the values of γ above 170° C, as deduced from formulations in a previous report [3]. From 195° to 374.15° C, inclusive, the values of L are directly obtained from the formulation of L in the previous report [3]. Corresponding values of γ in this range are in accord with the preferred values of β, as specified above.

The values of specific volume of saturated liquid, u, and of saturated vapor, u', are consistent with values of β, and γ through the thermodynamic relation, using the Clapeyron factor, TdP/dt.

For obtaining entropy in the range 100° to 374.15° C, use was made of the empirical formula for α given above and expressed in the differential form

$$\frac{d\alpha}{dt}=4.1744-\{1.878(t-130)^{2.1}-0.066(t-200)^{2.64}\}10^{-6}.$$

For convenience in integrating the function $\frac{d\alpha}{Tdt}$, this function was

formulated, using values from the $d\alpha/dt$ equation to obtain a new explicit function of temperature of the form

$$\frac{d\alpha}{Tdt}=\frac{4.1744}{T}+10^{-7}\{-0.0607(t-130)^2+0.0105(t-200)^{2.29}\},$$

which, by integration, becomes

$$\int_{t_1}^{t}\frac{d\alpha}{Tdt}dt=9.605095\log_{10}\frac{T}{T_1}$$
$$+10^{-7}\left[-0.020233(t-130)^3+0.003192(t-200)^{3.29}\right]_{t_1}^{t}$$

In this equation, however, values of $(t-130)^3$ are to be used only above 130° C. By using the calculated values of this integral, the value of entropy at 100° C as the constant of integration, and values of β/T, the values of $\Phi]^t_0$, entropy of saturated liquid at the temperature t, are determined. Values of $\Phi']^t_0$, entropy of saturated vapor, are determined by the addition of L/T.

Tables 1 and 2 contain the numerical values obtained as described in the foregoing text. For conversion from international joules per gram to International Steam Table Calories per gram, the factor 1 int. j/g=0.238891 IT Cal/g has been used.

It may appear that the compilation of these properties of saturated water and steam as described here is quite a patchwork. Simplicity, rationality, or orderliness of formulas have as yet eluded the inspiration of this group and its colleagues. However much care has been taken to insure that the tabulated values are smooth functions of temperature and that the different groups of NBS calorimetric data have been fairly interpreted to give a consistent and congruent compilation, which now supersedes earlier ones issued from this laboratory

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TABLE 1.—*Formulated data on saturated steam*

Temperature	α_0^t	β	γ	U_0^t	H_0^t	L	$T\frac{dP}{dT}$
°C	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/cm*^{3}
100	417. 63	1. 41	2257. 71	419. 03	2675. 33	2256. 30	1. 3495
105	438. 49	1. 66	2244. 70	440. 13	2683. 17	2243. 04	1. 5815
110	459. 34	1. 94	2231. 54	461. 27	2690. 87	2229. 60	1. 8441
115	480. 20	2. 26	2218. 22	482. 45	2698. 41	2215. 96	2. 1402
120	501. 06	2. 62	2204. 75	503. 67	2705. 80	2202. 13	2. 4725
125	521. 92	3. 03	2191. 10	524. 93	2713. 00	2188. 07	2. 8440
130	542. 77	3. 48	2177. 26	546. 25	2720. 02	2173. 78	3. 2578
135	563. 63	3. 99	2163. 24	567. 61	2726. 86	2159. 25	3. 7170
140	584. 49	4. 56	2149. 00	589. 04	2733. 47	2144. 44	4. 2248
145	605. 34	5. 19	2134. 55	610. 52	2739. 88	2129. 36	4. 7847
150	626. 20	5. 89	2119. 87	632. 07	2746. 05	2113. 98	5. 3999
155	647. 05	6. 66	2104. 95	653. 69	2751. 98	2098. 29	6. 0740
160	667. 89	7. 51	2089. 78	675. 39	2757. 66	2082. 27	6. 8105
165	688. 74	8. 44	2074. 34	697. 16	2763. 06	2065. 90	7. 6129
170	709. 57	9. 46	2058. 63	719. 02	2768. 19	2049. 17	8. 4850
175	730. 41	10. 57	2042. 63	740. 96	2773. 02	2032. 06	9. 4305
180	751. 23	11. 79	2026. 34	763. 01	2777. 55	2014. 55	10. 453
185	772. 05	13. 11	2009. 73	785. 15	2781. 77	1996. 63	11. 557
190	792. 86	14. 55	1992. 80	807. 40	2785. 65	1978. 25	12. 745
195	813. 66	16. 11	1975. 53	829. 76	2789. 21	1959. 42	14. 023
200	834. 46	17. 80	1957. 88	852. 25	2792. 32	1940. 08	15. 393
205	855. 24	19. 63	1939. 85	874. 86	2795. 08	1920. 22	16. 860
210	876. 01	21. 61	1921. 45	897. 60	2797. 45	1899. 84	18. 429
215	896. 77	23. 74	1902. 65	920. 50	2799. 40	1878. 91	20. 102
220	917. 51	26. 04	1883. 45	943. 54	2800. 95	1857. 41	21. 885

TABLE 1.—*Formulated data on saturated steam*—Continued

Temperature	$\alpha]_0^t$	β	γ	$H]_0^t$	$H']_0^t$	L	$T\frac{dP}{dT}$
°C	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/cm³*
225	938. 24	28. 52	1863. 82	966. 75	2802. 05	1835. 30	23. 782
230	958. 96	31. 18	1843. 76	990. 13	2802. 71	1812. 58	25. 797
235	979. 66	34. 04	1823. 24	1013. 70	2802. 89	1789. 20	27. 935
240	1000. 35	37. 12	1802. 24	1037. 46	2802. 58	1765. 12	30. 201
245	1021. 03	40. 42	1780. 75	1061. 43	2801. 76	1740. 33	32. 599
250	1041. 68	43. 96	1758. 73	1085. 63	2800. 40	1714. 77	35. 136
255	1062. 32	47. 76	1736. 16	1110. 08	2798. 47	1688. 40	37. 815
260	1082. 95	51. 84	1713. 01	1134. 78	2795 95	1661. 17	40. 642
265	1103. 55	56. 21	1689. 24	1159. 76	2792. 78	1633. 03	43. 624
270	1124. 14	60. 90	1664. 81	1185. 04	2788. 94	1603. 91	46. 765
275	1144. 72	65. 94	1639. 68	1210. 64	2784. 38	1573. 75	50. 074
280	1165. 27	71. 34	1613. 81	1236. 60	2779. 07	1542. 47	53. 556
285	1185. 80	77. 15	1587. 12	1262. 94	2772. 91	1509. 97	57. 219
290	1206. 32	83. 39	1559. 55	1289. 70	2765. 85	1476. 16	61. 071
295	1226. 81	90. 12	1531. 03	1316. 92	2757. 83	1440. 91	65. 120
300	1247. 29	97. 37	1501. 45	1344. 65	2748. 73	1404. 08	69. 375
305	1267. 75	105. 21	1470. 70	1372. 94	2738. 43	1365. 49	73. 846
310	1288. 18	113. 69	1438. 60	1401. 86	2726. 77	1324. 91	78. 545
315	1308. 60	122. 91	1405. 08	1431. 49	2713. 67	1282. 18	83. 484
320	1329. 00	132. 94	1370. 18	1461. 93	2699. 16	1237. 24	88. 677
325	1349. 37	143. 93	1333. 67	1493. 29	2683. 03	1189. 74	94. 14
330	1369. 73	156. 00	1295. 29	1525. 71	2665. 00	1139. 29	99. 89
335	1390. 06	169. 39	1254. 67	1559. 44	2644. 72	1085. 28	105. 96
340	1410. 37	184. 22	1211. 22	1594. 58	2621. 58	1027. 00	112. 37
345	1430. 67	200. 89	1164. 27	1631. 54	2594. 92	963. 38	119. 16

350	1450. 94	219. 99	1112. 84	1670. 92	2563. 77	892. 85	126. 38
355	1471. 19	242. 41	1055. 39	1713. 59	2526. 57	812. 98	134. 12
360	1491. 42	269. 81	989. 23	1761. 22	2480. 64	719. 42	142. 47
365	1511. 63	305. 62	908. 87	1817. 24	2420. 49	603. 25	151. 62
366	1515. 67	314. 42	890. 12	1830. 08	2405. 78	575. 70	153. 57
367	1519. 70	324. 04	870. 08	1843. 73	2389. 77	546. 04	155. 56
368	1523. 74	334. 66	848. 46	1858. 39	2372. 19	513. 80	157. 61
369	1527. 78	346. 58	824. 82	1874. 35	2352. 59	478. 24	159. 73
370	1531. 81	360. 24	798. 54	1892. 04	2330. 34	438. 30	161. 91
371	1535. 85	376. 40	768. 50	1912. 24	2304. 34	392. 10	164. 18
372	1539. 88	396. 59	732. 63	1936. 46	2272. 50	336. 04	166. 57
373	1543. 92	424. 66	685. 64	1968. 57	2229. 55	260. 98	169. 16
374	1547. 95	483. 49	598. 10	2031. 43	2146. 04	114. 61	172. 5
374.15	1548. 55	535. 1	535. 1	2083. 6	2083. 6	0. 00	173. 1

TABLE 2.—*Properties of saturated steam*

Temperature (° C)	Vapor pressure	Enthalpy			Specific volume		Entropy		Temperature
		Liquid	Vaporization	Vapor	Liquid	Vapor	Liquid	Vapor	
	kg/cm²	*IT Cal/g*	*IT Cal/g*	*IT Cal/g*	*cm³/g*	*cm³/g*	*IT Cal/g-°C*	*IT Cal/g-°C*	*° C*
0	0. 006228	0. 000	597. 3	597. 3	1. 00021	206288	0. 0000	2. 1865	0
5	. 008891	5. 028	594. 5	599. 5	1. 00008	147150	. 0182	2. 1554	5
10	. 012513	10. 040	591. 7	601. 7	1. 00035	106422	. 0361	2. 1256	10
15	. 017377	15. 043	588. 9	603. 9	1. 00095	77973	. 0536	2. 0972	15
20	. 023829	20. 040	586. 0	606. 1	1. 00184	57836	. 0708	2. 0699	20
25	. 032287	25. 033	583. 2	608. 3	1. 00301	43401	. 0877	2. 0438	25
30	. 043254	30. 024	580. 4	610. 4	1. 00442	32929	. 1043	2. 0188	30
35	. 057326	35. 015	577. 6	612. 6	1. 00605	25245	. 1206	1. 9948	35
40	. 075204	40. 006	574. 7	614. 7	1. 00789	19546	. 1367	1. 9719	40
45	. 097707	44. 997	571. 8	616. 8	1. 00993	15275	. 1525	1. 9499	45
50	. 12578	49. 990	569. 0	619. 0	1. 0121	12045	. 1681	1. 9287	50
55	. 16050	54. 984	566. 1	621. 1	1. 0145	9578	. 1834	1. 9084	55
60	. 20312	59. 981	563. 2	623. 2	1. 0171	7677. 6	. 1985	1. 8889	60
65	. 25501	64. 981	560. 2	625. 2	1. 0199	6201. 4	. 2134	1. 8701	65
70	. 31775	69. 984	557. 3	627. 3	1. 0228	5045. 3	. 2281	1. 8521	70
75	. 39307	74. 991	554. 3	629. 3	1. 0258	4133. 2	. 2426	1. 8347	75
80	. 48292	80. 002	551. 3	631. 3	1. 0290	3408. 3	. 2568	1. 8180	80
85	. 58943	85. 018	548. 3	633. 3	1. 0324	2828. 2	. 2709	1. 8018	85
90	. 71491	90. 039	545. 2	635. 3	1. 0359	2360. 9	. 2848	1. 7862	90
95	. 86192	95. 067	542. 1	637. 2	1. 0396	1982. 1	. 2986	1. 7712	95
100	1. 03323	100. 102	539. 0	639. 1	1. 0435	1673. 0	. 3122	1. 7566	100
105	1. 2318	105. 14	535. 8	641. 0	1. 0474	1419. 4	. 3256	1. 7426	105
110	1. 4609	110. 19	532. 6	642. 8	1. 0515	1210. 1	. 3388	1. 7289	110
115	1. 7239	115. 25	529. 4	644. 6	1. 0558	1036. 5	. 3519	1. 7157	115
120	2. 0245	120. 32	526. 1	646. 4	1. 0603	891. 71	. 3649	1. 7029	120

125	2. 3666	125. 40	522. 7	648. 1	1. 0649	770. 43	. 3777	1. 6905	125
130	2. 7544	130. 49	519. 3	649. 8	1. 0697	668. 32	. 3904	1. 6784	130
135	3. 1923	135. 60	515. 8	651. 4	1. 0747	582. 00	. 4029	1. 6667	135
140	3. 6848	140. 72	512. 3	653. 0	1. 0798	508. 66	. 4154	1. 6553	140
145	4. 2369	145. 85	508. 7	654. 5	1. 0851	446. 12	. 4277	1. 6442	145
150	4. 8535	151. 00	505. 0	656. 0	1. 0906	392. 57	. 4399	1. 6333	150
155	5. 5402	156. 16	501. 3	657. 4	1. 0962	346. 55	. 4520	1. 6227	155
160	6. 3023	161. 34	497. 4	658. 8	1. 1021	306. 85	. 4640	1. 6124	160
165	7. 1457	166. 55	493. 5	660. 1	1. 1081	272. 48	. 4759	1. 6022	165
170	8. 0764	171. 77	489. 5	661. 3	1. 1144	242. 62	. 4877	1. 5923	170
175	9. 1006	177. 01	485. 4	662. 4	1. 1208	216. 60	. 4994	1. 5825	175
180	10. 225	182. 28	481. 3	663. 5	1. 1275	193. 85	. 5110	1. 5730	180
185	11. 456	187. 57	477. 0	664. 5	1. 1344	173. 90	. 5225	1. 5636	185
190	12. 800	192. 88	472. 6	665. 5	1. 1415	156. 35	. 5340	1. 5543	190
195	14. 265	198. 23	468. 1	666. 3	1. 1489	140. 88	. 5454	1. 5452	195
200	15. 857	203. 59	463. 5	667. 1	1. 1565	127. 19	. 5567	1. 5362	200
205	17. 585	209. 00	458. 7	667. 7	1. 1644	115. 05	. 5679	1. 5273	205
210	19. 456	214. 43	453. 9	668. 3	1. 1726	104. 265	. 5791	1. 5185	210
215	21. 478	219. 90	448. 9	668. 8	1. 1812	94. 650	. 5903	1. 5098	215
220	23. 659	225. 40	443. 7	669. 1	1. 1900	86. 062	. 6014	1. 5011	220
225	26. 007	230. 95	438. 4	669. 4	1. 1992	78. 372	. 6124	1. 4925	225
230	28. 531	236. 53	433. 0	669. 5	1. 2087	71. 472	. 6234	1. 4840	230
235	31. 239	242. 16	427. 4	669. 6	1. 2187	65. 267	. 6344	1. 4756	235
240	34. 140	247. 84	421. 7	669. 5	1. 2291	59. 674	. 6454	1. 4671	240
245	37. 244	253. 57	415. 8	669. 3	1. 2399	54. 625	. 6563	1. 4587	245
250	40. 560	259. 35	409. 6	669. 0	1. 2512	50. 056	. 6672	1. 4503	250
255	44. 097	265. 19	403. 3	668. 5	1. 2631	45. 912	. 6782	1. 4418	255
260	47. 866	271. 09	396. 8	667. 9	1. 2755	42. 149	. 6891	1. 4334	260
265	51. 875	277. 06	390. 1	667. 2	1. 2886	38. 723	. 7000	1. 4249	265
270	56. 137	283. 09	383. 2	666. 3	1. 3023	35. 599	. 7109	1. 4163	270
275	60. 660	289. 21	376. 0	665. 2	1. 3168	32. 745	. 7219	1. 4077	275
280	65. 457	295. 41	368. 5	663. 9	1. 3321	30. 133	. 7328	1. 3990	280
285	70. 539	301. 70	360. 7	662. 4	1. 3483	27. 738	. 7439	1. 3902	285
290	75. 917	308. 10	352. 6	660. 7	1. 3655	25. 537	. 7550	1. 3812	290
295	81. 603	314. 60	344. 2	658. 8	1. 3839	23. 511	. 7662	1. 3720	295

TABLE 2.—*Properties of saturated steam*—Continued

Temperature	Vapor pressure	Enthalpy			Specific volume		Entropy		Temperature
		Liquid	Vaporization	Vapor	Liquid	Vapor	Liquid	Vapor	
°C	kg/cm²	ITCal/g	ITCal/g	ITCal/g	cm³/g	cm³/g	ITCal/g-°C	ITCal/g-°C	°C
300	87. 611	321. 22	335. 4	656. 6	1. 4036	21. 643	0. 7774	1. 3626	300
305	93. 952	327. 98	326. 2	654. 2	1. 4247	19. 916	. 7888	1. 3530	305
310	100. 64	334. 89	316. 5	651. 4	1. 4475	18. 316	. 8003	1. 3431	310
315	107. 69	341. 97	306. 3	648. 3	1. 4722	16. 831	. 8120	1. 3328	315
320	115. 12	349. 24	295. 6	644. 8	1. 4992	15. 451	. 8239	1. 3221	320
325	122. 95	356. 73	284. 2	641. 0	1. 5289	14. 167	. 8360	1. 3111	325
330	131. 18	364. 48	272. 2	636. 6	1. 562	12. 967	. 8484	1. 2996	330
335	139. 85	372. 54	259. 3	631. 8	1. 599	11. 841	. 8612	1. 2875	335
340	148. 96	380. 93	245. 3	626. 3	1. 639	10. 779	. 8743	1. 2745	340
345	158. 54	389. 76	230. 1	619. 9	1. 686	9. 771	. 8881	1. 2604	345
350	168. 63	399. 17	213. 3	612. 5	1. 741	8. 805	. 9025	1. 2448	350
355	179. 24	409. 36	194. 2	603. 6	1. 807	7. 869	. 9181	1. 2273	355
360	190. 42	420. 74	171. 9	592. 6	1. 894	6. 943	. 9354	1. 2069	360
365	202. 21	434. 12	144. 1	578. 2	2. 016	5. 995	. 9556	1. 1814	365
366	204. 64	437. 19	137. 5	574. 7	2. 048	5. 796	. 9602	1. 1754	366
367	207. 11	440. 45	130. 4	570. 9	2. 083	5. 593	. 9652	1. 1689	367
368	209. 60	443. 95	122. 7	566. 7	2. 123	5. 383	. 9704	1. 1619	368
369	212. 12	447. 77	114. 2	562. 0	2. 170	5. 164	. 9762	1. 1541	369
370	214. 68	452. 0	104. 7	556. 7	2. 225	4. 932	. 9825	1. 1453	370
371	217. 26	456. 8	93. 7	550. 5	2. 293	4. 681	. 9898	1. 1352	371
372	219. 88	462. 6	80. 3	542. 9	2. 38	4. 40	. 9986	1. 1230	372
373	222. 53	470. 3	62. 4	532. 6	2. 51	4. 05	1. 0102	1. 1067	373
374	225. 22	485. 3	27. 4	512. 7	2. 80	3. 47	1. 0332	1. 0755	374
374.15	225. 65	498.	0. 0	498.	3. 1	3. 1	1. 0524	1. 0524	374. 15

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1230

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ELECTROPHORESIS OF COLLAGEN

By John Beek, Jr. and Arnold M. Sookne

ABSTRACT

The electrophoretic mobilities of four collagens and a gelatin were measured. One collagen was prepared from a limed steer hide; the other three were from the fresh hide, tendons, and bones of a steer. The differences between the mobilities are explained in terms of differences in the amidonitrogen contents of the various preparations. The isoelectric point of the unlimed-hide collagen is at about 7.0 on the pH scale.

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I. INTRODUCTION

Some properties of collagens prepared from the hide, tendons, and bones of a steer are being compared in connection with research work on leather at the National Bureau of Standards, with the object of determining to what extent the white fibrous connective tissues of these structures are similar. This paper reports measurements of the electrophoretic mobilities of particles of these collagen preparations, a gelatin made from the hide collagen, and a collagen sample prepared from a limed steer hide.

II. EXPERIMENTAL MATERIALS AND PROCEDURE

The preparation of the collagens has been described in earlier publications [1, 2].[1] A Wiley mill was used to grind the samples. The gelatin was made from the unlimed-hide collagen by heating in water for 18 hours at 90° C.

In measuring the mobilities, the procedure described by Moyer [3] was followed in detail. Four types of buffer mixtures were used, namely, acetic acid with sodium hydroxide, and hydrochloric, phosphoric, and boric acids with potassium hydroxide. The ionic strength of all the buffers used was 0.02 molar. The acidities of the suspensions were measured with a glass electrode, the scale being fixed with reference to a value of 4.01 for the pH of a 0.05 molar solution of potassium acid phthalate.

The mobilities of gelatin were measured using suspensions of particles of Pyrex laboratory glass in solutions containing 0.01 percent of gelatin. Preliminary experiments at two acidities showed that, as the concentration of gelatin was increased beyond this value, there was no further change in the mobility of the particles.

[1] Figures in brackets indicate the literature references at the end of this paper.

At least 10 times of transit were measured for each suspension studied, the mean time being used for the calculation of the mobility. The measurements were made at 25° C.

The amidonitrogen contents of the collagen preparations were compared by hydrolyzing samples in 0.1 N hydrochloric acid for 20 hours at 100° C, neutralizing the solutions, and distilling the ammonia in the presence of an excess of magnesium oxide. As the amount of ammonia obtained varies with the conditions of hydrolysis and distillation [4], the results have no absolute significance. It is assumed here that the differences between results obtained under the same experimental conditions probably give a measure of the differences between the amounts of amidonitrogen in the several samples.

III. RESULTS AND DISCUSSION

The results of the determinations of mobility are shown in figure 1. The relatively large vertical scale in this figure was used because of the small slopes of the curves for the collagen preparations.

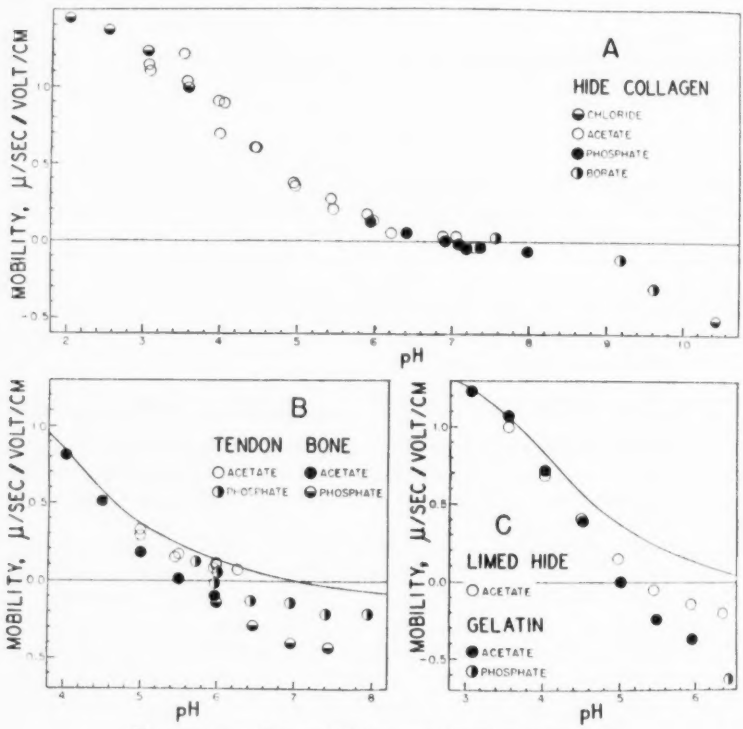

FIGURE 1.—*The mobilities as a function of acidity.*

Smooth curves are used in *B* and *C* to represent the mobility of the unlimed-hide collagen in order to avoid confusing these graphs with a large number of points.

The divergence of the mobilities at the lower acidities is qualitatively explained by the differences between the amidonitrogen contents of the various preparations, with the possible exception of the pair consisting of tendon and unlimed hide. The amidonitrogen

contents of the tendon, bone, and limed-hide collagens are lower than that of the unlimed-hide collagen by 0.1, 0.6, and 0.6 percent of the total nitrogen, respectively. This decrease in the amidonitrogen content is accompanied by an increase in the number of free carboxyl groups, which in turn has the effect of increasing the net negative charge, if the acidity of the suspension is such that the free carboxyl groups are ionized to a considerable extent.

With regard to the isoelectric points, it may be pointed out that liming had the effect of shifting the isoelectric point of the hide collagen from near 7 to about 5.3 on the pH scale. The gelatin used in this work has a less acid isoelectric point, namely 5.0, than those for which measurements are reported in the literature [5, 6], presumably because no acid or alkali was used in its preparation from the collagen. Thus, it may be seen that the electrophoretically determined isoelectric point of a sample of collagen or gelatin depends on the processes used in its preparation.

In conclusion, three points should be emphasized. First, if it is assumed that all the collagens used were the same in their natural states, the relations among their mobilities are satisfactorily explained by the effect of the treatments used in "purifying" the samples. Secondly, the acid treatment used in decalcifying the bone collagen and the alkaline treatment used in depilating the limed hide produced materials which are closely similar with respect to their electrophoretic mobilities. Finally, the effect on the mobility produced in the formation of gelatin from hide collagen appears to be similar to the effect produced in the bone and limed-hide collagens by the acid and alkaline treatments.

IV. REFERENCES

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[3] J. Bacteriology **31,** 531 (1936).
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[5] J. Chem. Soc. **1927,** 1250.
[6] J. Gen. Physiol. **15,** 575 (1932).

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1231

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THE SYSTEM PbO-B_2O_3-SiO_2

By R. F. Geller and E. N. Bunting

ABSTRACT

The system was investigated by well-known methods of quenching and petrographic examination. One ternary compound, $5PbO.B_2O_3.SiO_2$, was established. Over 90 percent of the system is occupied by the fields of $PbO.2B_2O_3$ and of SiO_2 and these fields lie predominantly under a two-liquid area. That portion of the system containing less than 60 percent of PbO is incomplete.

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I. INTRODUCTION

This report covers the results of studies on the system PbO-B_2O_3-SiO_2, a combination of oxides of interest primarily to manufacturers of glazed semiporcelain ware and of colors used for decorating ceramic whiteware and glass. These oxides are used also in the production of some glasses and vitreous enamels. The study is a part of the general investigation on systems containing PbO.[1]

The study of phase equilibria was limited, with the exception of a few melts, to mixtures containing more than 50 percent by weight of PbO because melts containing lower percentages are of very high viscosity. This property, in conjunction with the continued volatilization of B_2O_3 and of PbO at crystallizing temperatures, makes the attaining of even partial equilibrium in these viscous mixtures extremely difficult and time-consuming. Furthermore, it is believed evident that the ternary compound established by this study is the only one to form in the system.

[1] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS **13**, 237 (1934) RP705.
R. F. Geller and E. N. Bunting, J. Research NBS **17**, 277 (1936) RP911; and **18**, 585 (1937) RP995.

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II. EXPERIMENTAL PROCEDURE

1. PREPARATORY WORK

"End members" were sublimed litharge (PbO) containing 0.02 percent of total detected impurities, boric acid of reagent quality containing less than 0.01 percent of total detected impurities, and quartz crystal (SiO_2) containing 0.02 percent of nonvolatile residue on evaporation with HF and H_2SO_4.

All fusions were made in platinum, using electrically heated furnaces. One hundred and five melts were analyzed chemically and portions of these used in various combinations to obtain additional preparations. When preparing the melts, it was necessary to allow for volatilization of PbO and of B_2O_3 in order to approximate the desired composition.

The melts became increasingly unstable in air as the percentage of B_2O_3 exceeded about 30 and, for convenience, all preparations of melts and of crystallized samples were stored over P_2O_5.

To determine SiO_2, 0.5-g samples were fused with Na_2CO_3, dissolved in hot dilute HCl, evaporated almost to dryness, and the moist residue evaporated three times with 10 ml of CH_3OH saturated with HCl. This removed the B_2O_3. Silica was then determined in the usual way.

The PbO was determined as sulfate by double or, when necessary to obtain constant values, by triple evaporation with HF and H_2SO_4.

B_2O_3 was determined by difference.

All chemical analyses were made by A. S. Creamer.

2. TEST METHODS

Thermal studies were made by the quenching method.[2] The samples for quenching were held in capsules of platinum foil. Pt to Pt–Rh thermocouples were used for temperature measurements and were calibrated by observing the melting temperature of KCl (770.3° C). Usually air quenching was sufficient; otherwise the samples were dropped into CCl_4.

When working with compositions which crystallize readily, it is customary to quench from progressively lower temperatures and to note the temperature intervals within which crystals first appear. When, however, the melts are very viscous and the rates of crystallization extremely low, it is more feasible to obtain at least partial equilibrium at some temperature below the solidus and then quench from progressively higher temperatures. By this method, the investigator notes the temperature intervals within which the various crystal phases disappear.

The time required to crystallize the melts varied over a wide range. Compositions in which PbO exceeded 90 percent could be crystallized overnight, whereas many of those containing less than 80 percent were only partially crystallized after holding them several months at temperatures below the estimated solidus. In several instances, as illustrated in table 1 (for example, melts 110, 140, and 160), melts held at temperatures below the liquidus in the two-liquid area still contained two liquids. The time that melts could be held to attain equilibrium was limited in some cases by volatilization from the sample or by attack on the platinum capsules. For example, in the preliminary work some melts were held unnecessarily long and the index of refrac-

[2] F. C. Kracek, N. L. Bowen, and G. W. Morey, J. Phys. Chem. **33**, 1857 (1929).

tion of the glass, after remelting, or even the primary phase if the melt was near a boundary, would be different from that found for the same melt held for a shorter time. It was assumed that the composition had been changed by volatilization.

With the exception of a few of the compositions highest in PbO, samples of the previously crystallized melts were held at least overnight before each quench. Frequently it was necessary to compromise between the time required to reach complete equilibrium and attack on the capsule. Such attack resulted in the capsules becoming black and brittle; and frequently the melts contained a scattering of small, prismatic crystals which probably were composed in part of platinum.

TABLE 1.—*Some compositions at approximately 10-percent intervals in the silica and lead diborate fields*

Melt number	Composition			Held to crystallize		Treatment before quenching		Phases present
	PbO	B_2O_3	SiO_2	Time	Temperature	Time held	Temperature	
	Percent	*Percent*	*Percent*	*Days*	*°C*	*hr*	*°C*	
110	10.1	48.9	41.0	240	650			Two glasses, lower index<(1.47
120	20.0	39.7	40.3	90	800			Two glasses, lower index 1.47.
120						23	845	Two glasses.
120						46	850	Glass index 1.505.
130	30.2	29.3	40.5	90	800			Two glasses.
130						24	865	Do.
130						23	875	Glass, index 1.54.
140	40.4	19.7	39.9	106	600			Quartz and two glasses.
140						6	960	Tridymite and two glasses.
140						18	975	Glass, opalescent.
150	50.2	10.2	39.6	106	600			Quartz and glass
150						18	1070	Tridymite and glass.
150						5	1080	Glass, index 1.63.
160	10.2	59.5	30.3	260	650			$PbO.2B_2O_3$ and two glasses.
160						72	740	Do.
160						48	750	Two glasses, lower index<1.47.
160						48	760	Glass index, 1.485.
170	20.6	49.0	30.4	260	650			Minute crystals and two glasses.
170						48	750	$PbO.2B_2O_3$ and two glasses.
170						20	760	Two glasses.
170						48	800	Do.
170						48	820	Glass, index 1.505.
180	30.4	39.0	30.6	260	650			$PbO.2B_2O_3$ and two glasses.
180						72	750	Do.
180						72	770	Two glasses.
180						23	850	Do.
180						22	870	Glass, index 1.54.
200	50.2	19.9	29.9	91	800			Quartz and two glasses.
200						24	900	Tridymite and two glasses.
200						24	910	Two glasses, higher index 1.65.
210	60.1	10.3	29.6	107	600			Quartz and glass.
210						24	1025	Tridymite and glass.
210						47	1035	Glass, index 1.72.
250	40.2	39.6	20.2	30	600			Two glasses.
260	50.5	29.2	20.3	12	695			Two glasses, index—*a*, 1.75; *b*, 1.47.
270	60.4	19.4	20.2	122	490			Quartz and glass.
270						18	815	Do.
270						2	825	Glass, index 1.72.
280	69.9	10.2	19.9	122	490			Quartz, $PbO.SiO_2$ and glass.
280						1	625	Do.
280						1	630	Quartz and glass.
280						1	775	Do.
280						18	790	Glass, index 1.79.
330	50.2	39.8	10.0	13	650			Two glasses, upper index 1.76.
340	60.1	29.9	10.0	13	650			$PbO.2B_2O_3$ and two glasses.
340						23	735	$PbO.2B_2O_3$ and glass.
340						24	740	Glass, 1.72.
350	70.1	19.9	10.0	30	600			$PbO.2B_2O_3$ and glass.
350						18	680	Do.
350						18	685	Glass index, 1.80.

The petrographic microscope was used to determine the phases in quenched samples. Identification of the crystalline phases was limited practically to the establishment of optical character and indices of refraction. Samples in solid media (ranging in index of refraction from 1.74 to 2.58) were examined by means of white light passed through a No. 25 Wratten filter, which type of illumination had been used in determining the indices of the media.[3]

X-ray diffraction patterns were made and interpreted by H. F. McMurdie. Samples were pulverized and mounted with collodion on glass rods 0.1 to 0.2 mm in diameter. The sample, placed at the center of a cylindrical camera with a radius of 5.70 cm, was rotated constantly during 17 hours' exposure. Radiation was produced by a gas-type tube with copper target, the tube being operated at approximately 40 kv and 4 to 5 ma. The Kβ-radiation was removed by a nickel filter at the entrance to the camera.

III. BINARY SYSTEMS OF COMPONENTS

The systems PbO-SiO_2 and PbO-B_2O_3 have been described by the authors.[4]

The system B_2O_3-SiO_2 has been investigated by Greig [5] and by Cousen and Turner,[6] who believe these oxides as glasses to be completely miscible in all proportions.

Since the report by the authors on the system PbO-B_2O_3, the crystallization of B_2O_3 has been accomplished [7] and its properties reported.[8]

IV. TERNARY COMPOSITIONS AS GLASSES

The thermal expansion, softening temperature by interferometer method, and relative solubility of compositions at 10-percent intervals have been reported.[9] Index of refraction values of the same melts, and additional ones in the high PbO region, are shown in figure 1. In the majority of cases the melts were either too viscous to permit "fining" to clear, uniform glasses, or they were opalescent because of separation into two liquids. Consequently, the values given in the figure represent the average indices.

The value for B_2O_3 glass is taken from the work of Morey and Merwin [10] and the value for SiO_2 glass from Tilton and Tool.[11]

V. THE TWO-LIQUID AREA

At least 90 percent of the system is occupied by the fields of SiO_2 and of $PbO.2B_2O_3$, and the greater portion of both these fields lies under a region of liquid immiscibility (fig. 2). Very little is known about the two-liquid area. Its boundaries, as indicated in figure 2, were estimated largely by whether or not the melts developed opaqueness without the development of crystals discernible either micro-

[3] These media had been prepared, during another investigation, by L. T. Brownmiller, using piperine and iodides, and sulfur and selenium mixtures, as recommended by Esper S. Larsen and Harry Berman in United States Geological Survey Bulletin 848 (1934).
[4] See footnote 1.
[5] J. W. Greig, Am. J. Sci. [5] **13**, 133 (1927).
[6] A. Cousen and W. E. S. Turner, J. Soc. Glass Tech. **12**, 169 (1928).
[7] L. McCulloch, J. Am. Chem. Soc. **59**, 2650 (1937).
[8] F. C. Kracek, G. W. Morey, and H. E. Merwin, Am. J. Sci. [5] **35A**, 143 (1938).
[9] R. F. Geller, E. N. Bunting, and A. S. Creamer, J. Research NBS **20**, 57 (1938) RP 1064.
[10] G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. **58**, 2248 (1936).
[11] L. W. Tilton and A. Q. Tool, BS, J. Research **3**, 619 (1929) RP112.

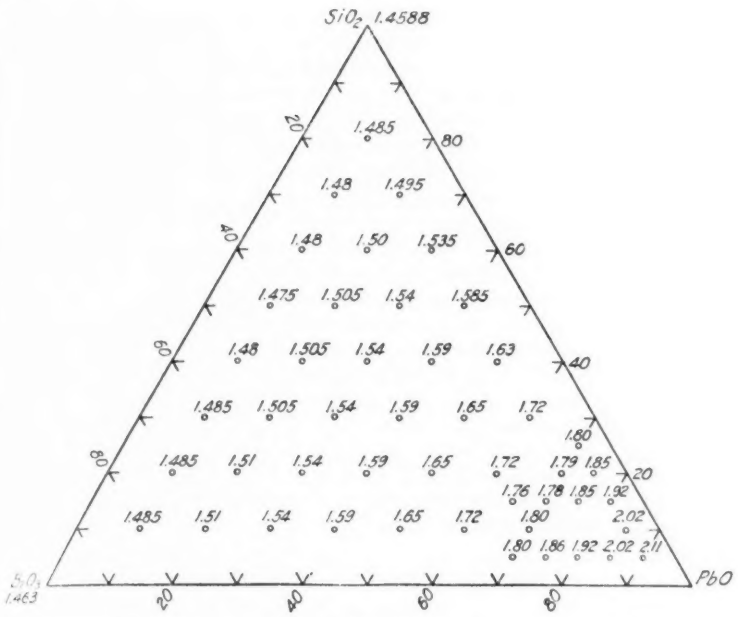

FIGURE 1.—*Average indices of refraction of compositions as glasses.*

Values below 1.72 are believed accurate within ±0.005, and higher values within ±0.01.

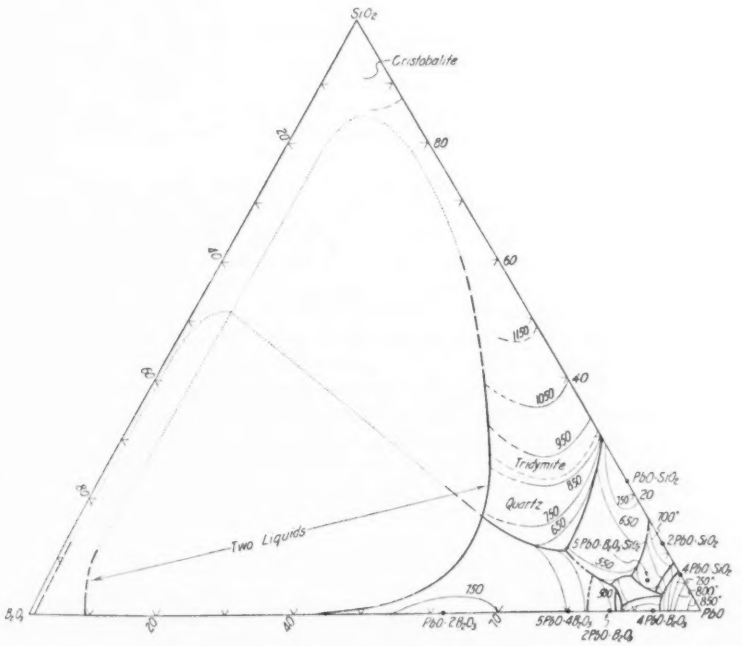

FIGURE 2.—*The system* $PbO-B_2O_3-SiO_2$.

scopically or with X-rays. In these cases the opaqueness was caused by the intimate mixture, or emulsion, of the two glasses.

In that portion of the area indicated as lying over the $PbO.2B_2O_3$ field, identifiable crystals of this phase were developed after holding melts for several weeks or months at favorable temperatures (table 1). Also, the two liquids in several compositions separated sufficiently to permit the determination of their indices. The lower index, about 1.47, would support the assumption that the two-liquid area extends to compositions containing less than 10 percent of PbO. Since all glasses on the same PbO "level" have about the same indices (fig. 1), it is evident that the indices of two immiscible glasses do not indicate the direction of isotherms within the two-liquid area.

The liquidus surface of the two-liquid area in the $PbO.2B_2O_3$ field is apparently very flat, dropping from 742° in the PbO-B_2O_3 system to about 730° at the $PbO.2B_2O_3$-SiO_2 boundary. Proceeding beyond this boundary into the SiO_2 field, the surface must rise sharply as indicated by the isotherms extending from the PbO-SiO_2 system.

The data (table 1) indicate also that the upper surface of the two-liquid area over the $PbO.2B_2O_3$ field, and at the 30-percent SiO_2 level, is about 10° C above the liquidus at the 10-percent PbO level, 50° C above at the 20-percent PbO level, and 100° C above at the 30-percent PbO level.

VI. FIELDS OF STABILITY

1. SiO_2 AND $PbO.2B_2O_3$

That portion of the SiO_2 field which is known not to be under the two-liquid area extends as a narrow belt, along the PbO-SiO_2 side of the diagram, to the SiO_2-$PbO.SiO_2$-$PbO.2B_2O_3$ quintuple point. Because of the practical difficulty of obtaining complete crystallization in the proximity of this point, its location was estimated from the contour of the liquidus and placed at 540° ± 10° C and 75 percent of PbO, 15 percent of B_2O_3, and 10 percent of SiO_2. Typical data for some of the compositions at approximately 10-percent intervals are given in table 1.

No information was obtained on how far that portion of the $PbO.2B_2O_3$ field near the 100-percent B_2O_3 apex, and not under the two-liquid area, extends into the system. In a report on liquid immiscibility in the system CaO-B_2O_3-SiO_2, Morey [12] has suggested a possible relation of primary fields adjacent to the B_2O_3-SiO_2 side in that system. The same general arrangement of phase relations may exist in the comparable portion of the PbO-B_2O_3-SiO_2 system. In figure 2 the heavy broken lines show experimentally determined trends, whereas the light dotted lines indicate possible limits of the fields.

The boundary for the $PbO.2B_2O_3$ field falls from about 730° C at its intersection with the two-liquid area, through the SiO_2-$PbO.SiO_2$-$PbO.2B_2O_3$ quintuple point, to the $PbO.SiO_2$-$PbO.2B_2O_3$-$5PbO.4B_2O_3$ quintuple point at 527° C and 81 percent of PbO, 13 percent of B_2O_3, and 6 percent of SiO_2. The boundary then rises to the PbO-B_2O_3 system at 548° C and 83 percent of PbO.

Near the $PbO.SiO_2$-$PbO.2B_2O_3$-$5PbO.4B_2O_3$ quintuple point, shown to better advantage in figure 3, is a small area, *A*, within which an unidentified crystal phase was primary in two compositions. It appeared in no other compositions, although several in adjacent

[12] G. W. Morey and Earl Ingerson, Am. Mineral. **22**, 37 (1937).

portions of this system begin to crystallize within the temperature range in which phase *A* was found in the binary system (530° to 580° C).[13] It is believed to be a metastable form either of $PbO.2B_2O_3$ or of $5PbO.4B_2O_3$. Adjacent boundaries are shown in broken lines to indicate that the field of phase *A* may or may not be completey enclosed by the field of $PbO.2B_2O_3$. It should be noted that the secondary phase in melt 445 (fig. 3), which phase appears on cooling at

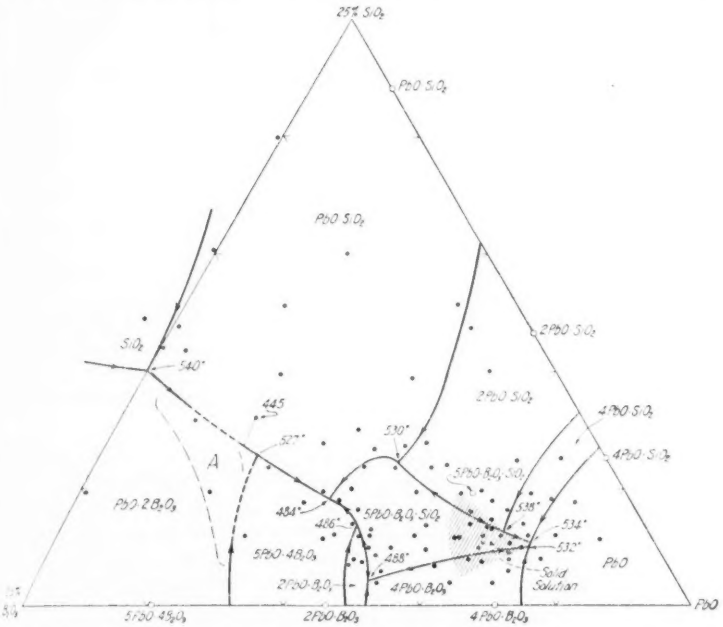

FIGURE 3.—*That portion of the system* $PbO\text{-}B_2O_3\text{-}SiO_2$ *containing over 75 percent (by weight) of* PbO.

the intersection of the dotted line (crystallization curve) with the $PbO.SiO_2$ boundary, is $PbO.2B_2O_3$, and therefore field *A* does not extend to the quintuple point at 527° C.

2. $5PbO.B_2O_3.SiO_2$

Pentalead borosilicate (89.58 percent of PbO, 5.59 percent of B_2O_3, and 4.83 percent of SiO_2) is the only ternary compound found in this system. It melts incongruently at 551° C to form $2PbO.SiO_2$ and liquid.[14] Its field, although small (fig. 3), is bounded by the fields of seven other compounds, and its boundary includes the three eutectic points and all of the quintuple points, except the two already discussed, which are found in this system (table 2).

Optically the prismatic crystals of $5PbO.B_2O_3.SiO_2$ are nearly, or quite, uniaxial; character is negative; and the indices of refraction are ϵ (or α) 2.04 ± 0.005, and ω (or β and γ) 2.085 ± 0.005. At tempera-

[13] This is the same phase which appeared in the $PbO\text{-}B_2O_3$ system. R. F. Geller and E. N. Bunting, J. Research NBS **18**, 585 (1937) RP995.

[14] It is interesting that the only ternary compound found at the liquidus in the system lime-boric oxide-silica has the same molecular ratio (see E. P. Flint and Lansing S. Wells, J. Research NBS **17**, 727 (1936) RP941).

tures above approximately 535° C, and in compositions occupying the central and "high-lead" portions of the shaded area (fig. 3), these crystals have indices of refraction equal to 2.09 (min) and 2.12 (max). In compositions at the "low-lead" fringe of the area, and at temperatures between about 535° and 545° C, the indices were found to be about 2.08 (min) and 2.10 (max). The interference figure appeared the same for all of these crystals. That the changes in indices result from solid solution and do not evidence polymorphism in the ternary compound is shown by the results of McMurdie's examinations:

TABLE 2.—*Invariant points in the system lead borosilicate*

	Composition by weight			Type	Temperature
	PbO	B_2O_3	SiO_2		
	Percent	*Percent*	*Percent*		°C
SiO_2-PbO.SiO_2-PbO.$2B_2O_3$	75	15	10	Quintuple	540±10
PbO.SiO_2-PbO.$2B_2O_3$-5PbO.$4B_2O_3$	81	13	6	do	527±5
5PbO.B_2O_3.SiO_2-PbO.SiO_2-5PbO.$4B_2O_3$	84.5	11.0	4.5	Eutectic	[a] 484±2
5PbO.B_2O_3.SiO_2-PbO.SiO_2-2PbO.SiO_2	86.3	7.6	6.1	Quintuple	530±3
5PbO.B_2O_3.SiO_2-2PbO.SiO_2-4PbO.SiO_2	91.5	5.3	3.2	do	538±2
5PbO.B_2O_3.SiO_2-4PbO.SiO_2-PbO	92.7	4.5	2.8	do	[a] 534±2
5PbO.B_2O_3.SiO_2-4PbO.B_2O_3-PbO	92.7	4.8	2.5	Eutectic	[a] 502±2
5PbO.B_2O_3.SiO_2-4PbO.B_2O_3-2PbO.B_2O_3	87.5	11.4	1.1	do	[a] 488±2
5PbO.B_2O_3.SiO_2-2PbO.B_2O_3-5PbO.$4B_2O_3$	86.0	10.6	3.4	Quintuple	[a] 486±2

[a] Under the particular conditions of test used in this investigation, this value is believed to be reproducible within ±1° C.

The X-ray diffraction pattern of the crystallized 5PbO.B_2O_3.SiO_2 composition and the composition in the central portion of the solid solution area (crystals and glass) indicated an orthorhombic structure with $a_0=5.14$ A, $b_0=5.68$ A, and $c_0=6.24$ A. This gives an axial ratio of 0.905:1:1.10. The spacings and the estimated relative intensities are given in table 3. Column 4 gives the spacing calculated from the unit cell size as given above. The lines produced by planes with d less than 1.552 were rather faint owing to absorption of the radiation by the Pb.

TABLE 3.—*Interplanar spacings of* 5PbO.B_2O_3.SiO_2

d_{hkl} observed	Relative intensity [a]	Miller indices	d_{hkl} calculated	d_{hkl} observed	Relative intensity [a]	Miller indices	d_{hkl} calculated
A			*A*	*A*			*A*
4.19	*S*	011	4.19	2.07	*W*	003	2.08
3.96	*S*	101	3.97	1.98	*M*	202	1.98
3.25	*S*	111	3.25	1.928	*M*	103	1.932
3.12	*S*	002	3.12	1.867	*M*	212	1.868
2.84	*SS*	020	2.84	1.832	*S*	113	1.831
2.75	*M*	012	2.73	1.782	*SS*	130	1.777
2.30	*WW*	121	2.29	1.650	*WW*	301	1.650
2.19	*WW*	211	2.19	1.631	*WW*	222	1.631
2.11	*W*	022	2.10	1.552	*M*	132	1.550

[a] S, strong; SS, very strong; M, medium; W, weak; WW, very weak.

3. PbO.SiO_2, 2PbO.SiO_2, 4PbO.SiO_2, PbO, 4PbO.B_2O_3, 2PbO.B_2O_3 AND 5PbO.$4B_2O_3$

There are no unusual features about the fields for these compounds. The boundary curves, and the important temperatures and invariant points, may be obtained from figures 2 and 3, and table 2.

VII. SUMMARY

The compositions studied have some potential value to those interested in stable, low-melting glasses of high refractive index. Their value as ceramic glazes is limited and has been discussed in a previous publication (see footnote 9).

Phase relations within the system resemble those for the system $CaO-B_2O_3-SiO_2$ in two particulars; the two-liquid area covers a large portion of the diagram; and the one ternary compound possessing a field in each system has the same molecular ratio (5:1:1).

The new compound, $5PbO.B_2O_3.SiO_2$, melts incongruently at 551° C to form $2PbO.SiO_2$ and liquid. It is negative in character and the X-ray pattern shows orthorhombic, and therefore biaxial, structure. Interference figures indicated the crystals to be nearly, or quite, uniaxial. The indices of refraction are ϵ (or α) 2.04 ± 0.005 and ω (or β and γ) 2.085 ± 0.005. Throughout a small area it forms solid solutions as a result of which the indices are raised to 2.10 (min) and 2.12 (max), but an X-ray pattern of solid solution crystals having these indices did not show a measurable shift as compared with the pattern for the compound composition.

The liquidus of the lowest-melting eutectic is at 484° C and 84.5 percent of PbO, 11.0 percent of B_2O_3, and 4.5 percent of SiO_2.

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PARTICLE SIZE AND PLASTICITY OF LIME

By Dana L. Bishop

ABSTRACT

Particle-size distributions and Emley plasticity values were determined on 25 hydrated limes. The geometric weight-mean diameters varied from 2.9 to 7.8 microns. There was no relation between their particle-size distributions down to 2 microns and their Emley plasticity values. Hydrated limes having very similar particle-size distributions had widely different plasticities. Particle-size measurements down to about 1 micron were made on quicklime putties prepared by hydrating quicklimes with an excess of water. Putties prepared in such a manner were very much finer than the commercial hydrated limes. There was also no relation between the distributions down to 1 micron and the Emley plasticity values of the quicklime putties. Limes having the same calculated specific surface may have widely different particle-size distributions. It is possible that the size distribution of the material finer than 2 microns may be the determining factor in the plasticity of limes.

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I. INTRODUCTION

Very few data are available concerning the particle-size distribution of commercial hydrated limes, especially for that portion which is finer than 10 microns. For this reason and because of the recent interest in the plasticity of lime, these data relating to the particle size and Emley plasticity values of hydrated limes and quicklime putties are presented.

II. MEASUREMENTS

1. EMLEY PLASTICITY VALUES

Plasticity measurements of the hydrated limes and quicklime putties were made with the Emley plasticimeter, the instrument commonly used in the lime industry to measure plasticity.[1] The limes were

[1] SS-L-351, Federal Specification for Lime; Hydrated (for) Structural Purposes. Also Standard Specifications for Hydrated Lime for Structural Purposes, ASTM Designation C-6-31, Am. Soc. for Testing Materials, Standards, pt. 2, Non-Metals, p. 30 (1936).

made into stiff putties with water and allowed to soak overnight, after which they were brought to standard consistency by the gradual addition of water accompanied by vigorous stirring, thus obtaining maximum plasticity.

2. PARTICLE SIZE

The particle-size measurements reported in this paper were made by a method previously described.[2] This method consists essentially in weighing the lime as it settles out of suspension in a liquid, and calculating the particle-size distribution from the sedimentation record. Anhydrous butanol was used as a dispersion medium. This medium was chosen instead of water because it gives better dispersion of the lime. When lime is dispersed in water, agglomeration takes place, which alters the rate of sedimentation very much and would yield erroneous sedimentation data. In dilute suspensions in water much of the finer fraction is also lost through the interaction of the lime and carbon dioxide, with consequent solution and reduction in size of some of the particles. This seriously affects the particle-size indications, especially of the finer sizes. Sedimentation measurements were therefore made on dry hydrated lime after dispersing it in butanol with the aid of a stirring device.

III. PARTICLE-SIZE DISTRIBUTION

The sedimentation data of the hydrated limes indicated that many of them contained large amounts of very fine material. This fine material settled so slowly that it was impractical to obtain a complete sedimentation curve. Hence the sedimentations were ordinarily continued only sufficiently long to give points on the distribution curve down to about 2 microns for the hydrated limes and about 1 micron for quicklime putties.

In order to calculate any of the constants, such as mean diameter or surface area, which are used to describe a distribution, it was necessary to make some assumption regarding the distribution of the material below 2 microns in size. Hatch and Choate [3] have shown that the particle-size distribution of certain materials is such that if on logarithmic-probability paper the particle diameters are plotted on the logarithmic scale and the cumulative percentages of the total number of particles on the probability scale, the points fall on a straight line.[4] It can be shown that if a distribution is of this nature, the percentage by weight coarser than each size can be plotted instead of the number of particles, and these points will likewise fall on a straight line. The cumulative weight distribution of each of the 25 hydrated limes of this investigation was plotted on logarithmic-probability paper and in each case the points fell very close to a straight line (see fig. 1). It was therefore assumed in obtaining the geometric mean

[2] D. L. Bishop, BS J. Research **12**, 175 (1934) RP642.

[3] T. Hatch and S. P. Choate, *Statistical description of particle size of nonuniform substance*, J. Frank. Inst. **207**, 369 (1929).

[4] A straight line on such paper represents a distribution following the law

$$yd\,(\ln x) = \frac{1}{\sqrt{2\pi}\,\ln\lambda}\, e^{-\frac{\ln^2 x/g}{2\ln^2\lambda}}\, d\,(\ln x)$$

that is, the logarithm of x is distributed normally.

diameters, the geometric standard deviation,[5] and the specific surfaces that for each lime the diameter distribution of the particles smaller than 2 microns was represented by an extrapolation of the straight line fitted to the observed points for particles greater than 2 microns. Hatch and Choate have shown how for such a straight-line distribution the geometric mean and the standard geometric deviation can be

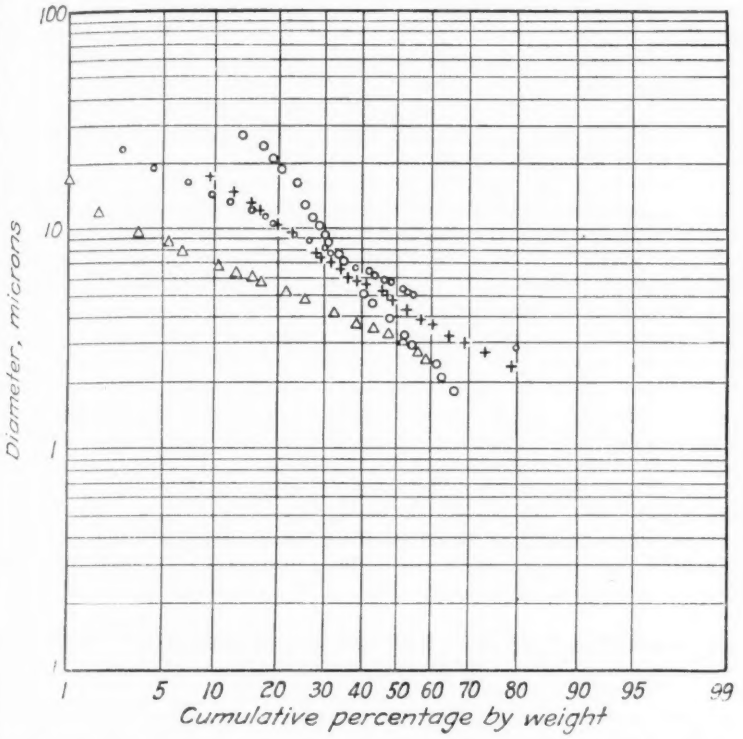

FIGURE 1.—*Particle-size distribution of four hydrated limes, showing straight line characteristics.*

obtained graphically and have pointed out that these two constants completely describe the distribution. For such a distribution the geometric weight-mean diameter, g, is that diameter which is exceeded by particles representing half the total weight of material. On a chart such as figure 1 this mean diameter can be read from the ordinate, and corresponds to the position at which a straight line through the plotted points crosses the vertical line representing a cumulative percentage of 50. (The straight lines were fitted by inspection.) The standard geometric deviation, λ, is a measure of the range of the particle sizes and for such a distribution is the ratio of the diameter of the 50-percent size to the diameter of the 16-percent size.

[5] The geometric-weight mean diameter, g, is by definition: antilog $\frac{\Sigma w_d \log d}{\Sigma w_d}$, where w_d is the weight of material of diameter d. The geometric standard deviation, λ, is by definition: antilog $\sqrt{\frac{\Sigma w_d (\log d - \log g)^2}{\Sigma w_d}}$.

It can be shown that for such a straight-line distribution the specific surface is given by the formula

$$s=6\cdot\frac{\lambda^{\frac{1}{2}\log_e\lambda}}{\rho g}$$

where ρ is the density of the material. (It is assumed that the particles are spherical.) Therefore, the surface per gram can be computed directly from the values of g and λ, which have been obtained by simple graphical methods. It is of note that for such a distribution any other mean diameter, such as arithmetic-weight mean diameter, and surface mean diameter can be quickly calculated from the value of g and λ. All the distribution constants given in table 1 were obtained by the above method.

The fact that the limes followed very closely the same empirical law of distribution in the entire region in which observations were made is strong evidence that the values reported as geometric mean, geometric standard deviation, and surface per gram are close to the correct values. However, the surface per gram depends to such a large extent upon the distribution of the particle diameters below 2 microns that this value is reported only to the nearest 1,000 cm^2/g. One should bear in mind that 50 percent by weight of the particles in each lime are of diameters smaller than the values reported as the geometric mean. Since the particle-size distribution was determined for more than 50 percent of the weight of every lime, no extrapolation was involved in obtaining the 50-percent size. It is only in identifying the 50-percent size as the geometric mean that extrapolation is involved.

Attention is called to the fact that limes of equal specific surface sometimes had widely different particle-diameter distributions. This is shown in table 1 by numbers 2 and 18, and 14 and 25.

IV. PARTICLE SIZE AND EMLEY PLASTICITY VALUES OF HYDRATES

Inspection of table 1 reveals that there is no relation between the particle-size constants and Emley plasticity values. Some of the nonplastic limes (limes having Emley plasticity values less than 200) are comparatively coarse and others are fine. Many of the plastic hydrates are coarse; but it is not likely that this is the determining factor, for the most plastic hydrate is likewise the finest of all. The distribution curves for two plastic and two nonplastic limes whose particle-size distributions are very similar are shown in figure 2. Not only are all four of these limes very similar but they may be considered as pairs made of a plastic and a nonplastic lime having almost identical distribution characteristics. Figure 3 shows the geometric weight-mean diameters, surface per gram, and Emley plasticity values of the hydrated limes. It is apparent from this graph that there is no correlation between Emley plasticity values and the geometric means or between such plasticity and specific surface. Even though table 1 and figures 2 and 3 do not indicate a relation between particle-size and Emley plasticity values, the fact that distributions below 2 microns were not actually measured leaves the possibility that the distribution of the material finer than 2 microns may be the determining factor in plasticity of limes.

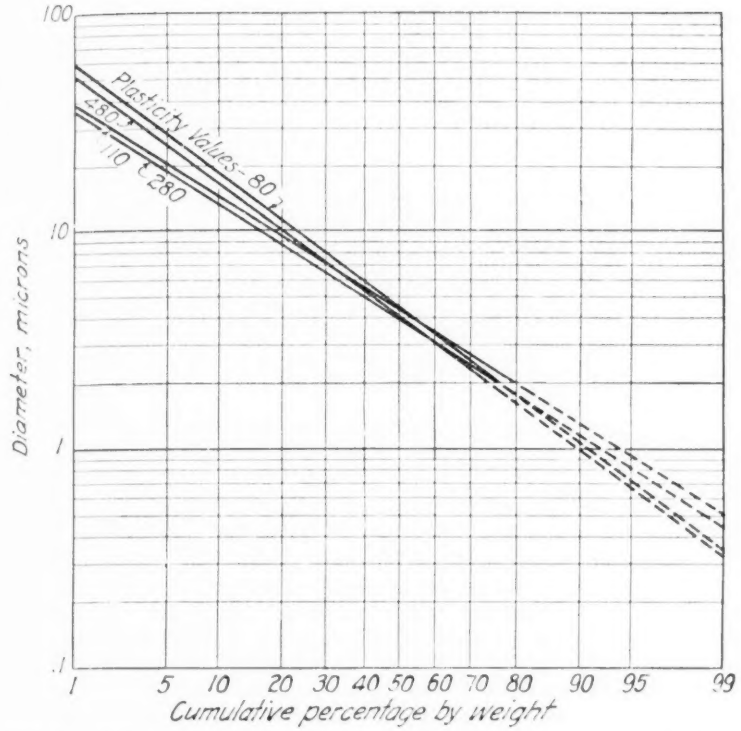

FIGURE 2.—*Particle-size distributions of four hydrated limes having widely varying Emley plasticity values but similar distribution.*

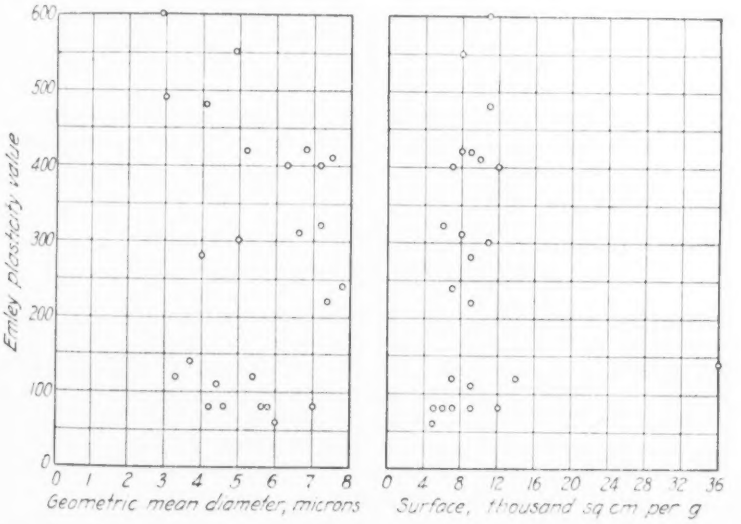

FIGURE 3.—*Emley plasticity values of hydrated limes plotted against their geometric mean diameters and surfaces.*

TABLE 1.—*Emley plasticity values and particle-size data for hydrated limes*

Lime number	Emley plasticity value	Geometric weight-mean diameter	Geometric standard deviation	Specific surface	Lime number	Emley plasticity value	Geometric weight-mean diameter	Geometric standard deviation	Specific surface
		Microns		*cm²/g*			*Microns*		*cm²/g*
1	60	6.0	1.9	5,000	14	300	5.0	3.4	11,000
2	80	4.2	3.1	12,000	15	310	6.6	3.6	8,000
3	80	4.6	2.7	9,000	16	320	7.2	2.8	6,000
4	80	5.6	2.2	6,000	17	400	6.3	2.8	7,000
5	80	5.8	2.4	7,000	18	400	7.2	4.9	12,000
6	80	7.0	2.2	5,000	19	410	7.5	4.5	10,000
7	110	4.4	2.5	9,000	20	420	5.2	2.9	8,000
8	120	3.3	3.0	14,000	21	420	6.8	4.4	10,000
9	120	5.4	2.2	7,000	22	480	4.1	3.0	11,000
10	140	3.7	6.1	36,000	23	490	3.0	10.5	110,000
11	220	7.4	3.9	9,000	24	550	4.9	2.6	8,000
12	240	7.8	3.4	7,000	25	600	2.9	2.1	11,000
13	280	4.0	2.5	9,000					

Other experiments were performed in an effort to find a relation between particle size and Emley plasticity values. An attempt was made to study the plasticity of various sized fractions of limes separated in an air elutriator.[6] There was some increase in plasticity with decrease in particle size, provided the lime was originally plastic, for separations that could be effected by blowing only a short time in the elutriator. Finer separations, requiring longer time in the elutriator, lost plasticity with increasing time of blowing, either through a slight amount of carbonation or possibly through the loss of an essential fraction of the lime during the elutriation. Such a loss could possibly occur through thermal precipitation in the cooling coils of the elutriator. Separations of nonplastic limes showed no change in Emley plasticity values for the various sized fractions.

A more successful method of making separations of the limes was the fractional sedimentation in ethanol. It was found that plastic hydrates could be treated with ethanol without affecting their plasticity. These plastic limes could be washed successively in water, ethanol, butanol, and kerosene, with the result that the limes would be plastic in each liquid. Plasticity measurements on fractions separated in ethanol indicated that for plastic limes the finer fractions of the sample were more plastic than the coarser ones. For nonplastic limes, however, there was no measurable difference in plasticity values for the various fractions.

V. PARTICLE SIZE AND EMLEY PLASTICITY VALUES OF QUICKLIME PUTTIES

Particle-size determinations were also made on putties which were obtained by hydrating quicklimes with an excess of water, so as to obtain a wet putty without forming an intermediate dry hydrate. Samples for particle-size determinations were prepared by removing the excess water from the putties with ethanol, and the ethanol in turn with butanol, after which they were dispersed in butanol. Considerable difficulty was encountered in measuring the particle size of these putties with the sedimentation apparatus because of their

[6] J. A. Swenson, Lacey A. Wagner, George L. Pigman, *Effect of granulometric composition of cement on the properties of pastes, mortars, and concrete*, J. Research NBS **14**, 419 (1935) RP777.

extreme fineness. Their sedimentation rates were so slow that even at small depths it was impossible to get complete sedimentation in a reasonable time. The data for these quicklimes are, therefore, presented only as a graph (fig. 4) because of the uncertainty in calculating distribution constants where such a large percentage of the material finer than 1 micron would have to be calculated from extrapolations. Even though the quicklime putties were very fine, they

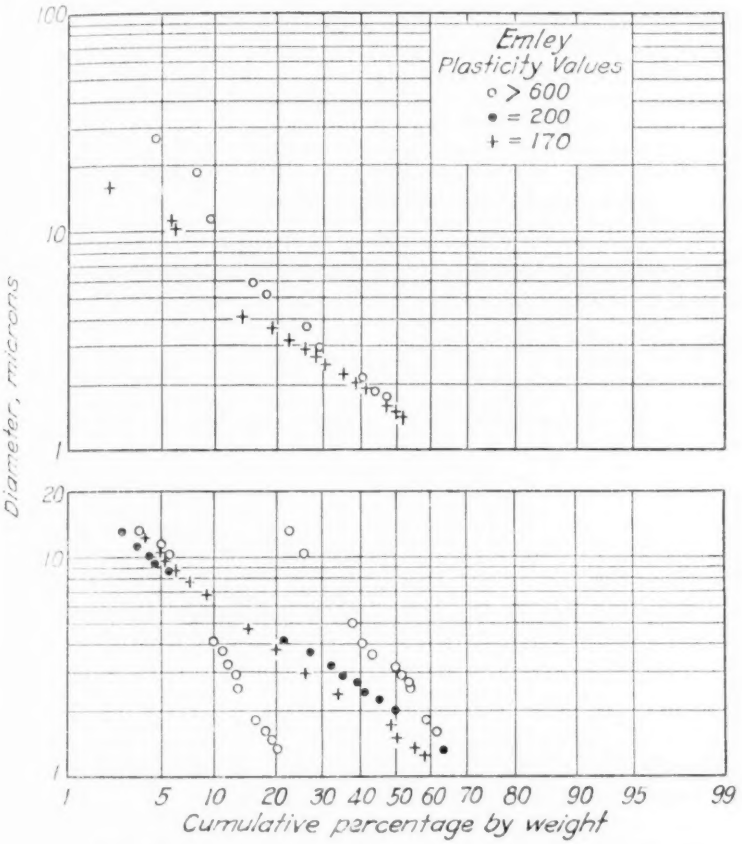

FIGURE 4.—*Particle-size distribution of quicklime putties.*

showed wide variations in particle size. Some contained considerable quantities of comparatively coarse particles, but all of them had a large percentage of material finer than 1 micron. Quicklimes, when hydrated with an excess of water, yield products which are very much finer than commercial dry hydrates.

The quicklime putties had Emley plasticity values such that some would be classed as nonplastic and some as very plastic limes. Here again the data (fig. 4) for the quicklimes indicate that there is no definite relation between Emley plasticity values and particle size, at least down to 1 micron.

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VI. SUMMARY

Measurements of the distribution of particle size down to 1 or 2 microns and of Emley plasticity values were made on commercial hydrated limes and on quicklime putties. There was no correlation between Emley plasticity values and the particle-size distributions, at least for the material coarser than 2 microns. Hydrated limes may have very similar particle-size distributions down to 2 microns and yet differ widely in their plasticity values. Quicklime putties prepared by hydrating quicklimes with an excess of water were very much finer than commercial hydrated limes. These likewise showed no correlation between such plasticity values and particle-size distributions down to 1 micron. Particle-size measurements of these limes indicated that limes may differ widely in particle-size distribution and yet have the same specific surface. It is possible that the size distribution of the material finer than 2 microns may be the determining factor in the plasticity of limes.

The writer is indebted to G. R. Gause for assistance in the mathematical treatment.

WASHINGTON, June 20, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1233

Part of Journal of Research of the National Bureau of Standards, Volume 23, August 1939

QUANTITATIVE FORMATION OF FURFURAL AND METHYLFURFURAL FROM PENTOSES AND METHYLPENTOSES

By Elizabeth E. Hughes and S. F. Acree

ABSTRACT

A procedure, previously reported, which gave quantitative production of furfural from xylose, was applied to arabinose and rhamnose. It consisted in rapid steam distillation of the pentose in 12-percent hydrochloric acid saturated with sodium chloride. Although the conversion of arabinose and rhamnose is slower than that of xylose, theoretical yields of furfural and methylfurfural, respectively, were obtained.

The effects of several salts in the distilling medium were also studied. The rates of production of furfural from xylose or arabinose in the presence of these salts and of methylfurfural from rhamnose in the presence of sodium chloride were obtained. Salts which caused the distillation temperature to go above 112° C increased the initial rate of formation of furfural but lowered the yields.

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I. INTRODUCTION

In a previous paper [1] [1] it was shown that conversion of xylose into quantitative yields of furfural may be accomplished by employing as the distilling medium a 12-percent solution of hydrochloric acid saturated with sodium chloride and by removing the aldehyde quickly from the solution with a rapid stream of steam. Since it was believed that this procedure might prove to yield quantitative amounts of furfural and methylfurfural when applied to other pentoses and methylpentoses, the study was extended to include arabinose and rhamnose.

The three pentoses derived from the pentosans xylan, araban, and rhamnosan are the sugars most commonly encountered in fibers and natural products. The pentoses are not determined as such, but are estimated from the amounts of furfural and methylfurfural obtained when the fibers are distilled with hydrochloric acid. As theoretical

[1] Figures in brackets indicate the literature references at the end of this paper.

yields of the aldehydes have not been obtained in the usual methods of distilling pentoses, empirical values have been adopted for the calculation of the pentosan content when these procedures are used.

The variations in yield of furfural obtained from xylose, depending upon the type of distillation employed (from 88 percent by the standard distillation procedure to 100 percent by our procedure), were discussed fully in the previous paper [1]. The conversion of arabinose is slower than that of xylose, with about 74 percent of the theoretical yield of furfural in the standard procedure. As stated in the earlier paper [1], the yields of furfural from xylose and arabinose and methylfurfural from rhamnose reported by Jolles [2] and Pervier and Gortner [3], which were practically theoretical, have not been duplicated by other workers, perhaps because of inaccuracies found later in the methods used for determining the aldehydes. Kullgren and Tyden [4], who saturated the hydrochloric acid with sodium chloride to give constant conditions for distillation, secured about the same yields as other workers obtain with the standard method.

It was the purpose of this investigation to obtain, if possible, theoretical yields of furfural and methylfurfural from the three pentoses and to adapt the procedure to the practical determination of pentosans. In an attempt to shorten the distillation period, the effects of some salts and of other reagents in the distilling medium were studied with xylose and arabinose. Xylose, the most easily converted sugar, was used chiefly for the experimentation. During this study the rates of production of furfural and methylfurfural from the three pentoses mentioned above were also obtained.

II. EXPERIMENTAL PROCEDURE

The distillation procedure was fully described in the paper on the quantitative formation of furfural from xylose [1]. It consisted essentially in distilling the pentose in a solution of 12-percent hydrochloric acid to which sodium chloride had been added and in using a rapid stream of steam to remove the aldehyde as soon as possible. A means of collecting the distillate without loss of furfural by volatilization was provided. This comprised an especially constructed apparatus having ground-glass joints, a diagram of which also was given in the earlier paper. By the use of an electrically controlled heater the distillation proceeded at 110° C at a rate of 200 ml of distillate every 30 minutes. More acid was added to the distillation flask through a separatory funnel as needed. The acidity of the distillate was adjusted to about 1 *N*, and the furfural and methylfurfural determinations were made by the bromine method at 0° C [5].

III. EXPERIMENTAL RESULTS AND DISCUSSION

1. STEAM DISTILLATION OF ARABINOSE

Samples of l-arabinose varying in amount from 0.05 to 0.2 g were treated by the procedure given above. The results of the distillations are given in table 1. The rate of production of furfural is shown in figure 1. It is apparent that practically theoretical yields may be obtained by this procedure if the distillation is continued until

the reaction is completed. The amounts of furfural in the last fractions of distillate are very small, but the bromine method is sufficiently sensitive for their determination. The amounts in the several fractions are added, and the values in the last column of table 1 show the total percentages of the theoretical amounts of furfural obtained.

TABLE 1.—*Yields of furfural from arabinose*

Weight of arabinose	Volume of distillate collected	Amount of bromine consumed	Weight of furfural found	Theoretical weight of furfural	Yields of furfural
g	*Liters*	*M-eq*	*g*	*g*	*Percent*
0.0513	2.2	0.679	0.0326	0.0328	99.4
0.0682	2.6	.910	.0437	.0436	100.2
0.1015	2.9	1.359	.0653	.0650	100.5
0.1048	4.6	1.399	.0672	.0671	100.1
0.1581	5.4	2.104	.1011	.1012	99.9
0.2029	3.4	2.623	.1260	.1299	97.0

2. STEAM DISTILLATION OF RHAMNOSE

The amounts of *l*-rhamnose (hydrate) used were 0.05 to 0.2 g. In the procedure used for the conversion of xylose and arabinose, the heat was applied to the flask containing the distilling solution and the

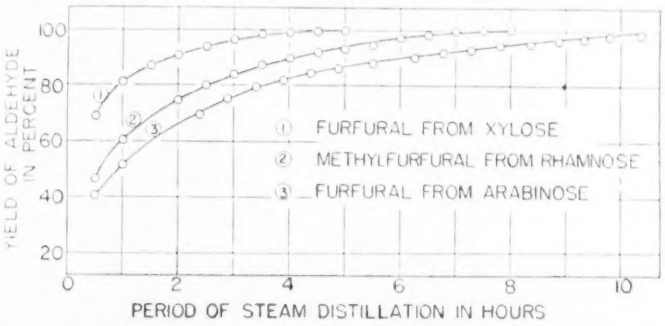

FIGURE 1.—*Rate of formation of aldehydes from pentoses by steam distillation in 12-percent hydrochloric acid saturated with sodium chloride.*

steam was not introduced until the temperature of the solution reached about 100° C. For rhamnose it was found necessary to modify this procedure slightly, as the first experiments gave yields 3 to 5 percent low, and the first fraction of distillate was very light pink, instead of being colorless. Since it seemed probable that some of the methylfurfural formed during the first period of heating had polymerized before being removed, the steam was introduced as soon as heat was applied to the solution. A colorless distillate was then obtained, and the sum of the fractions gave practically theoretical yields. The rate of production of methylfulfural by this method is shown with the other curves in figure 1, and the total yields of methylfurfural are given in table 2.

TABLE 2.—*Yields of methylfurfural from rhamnose (hydrate)*

Weight of rhamnose (hydrate)	Volume of distillate collected	Amount of bromine consumed	Weight of methylfurfural found	Theoretical weight of methylfurfural	Yields of methylfurfural
g	*Liters*	*M-eq*	*g*	*g*	*Percent*
0.0500	1.6	0.783	0.0308	0.0302	101.9
0.0733	2.2	1.111	.0437	.0443	98.6
0.0831	3.6	1.271	.0500	.0502	99.5
0.0980	3.2	1.528	.0601	.0592	101.4
0.1102	2.5	1.716	.0674	.0666	101.2
0.2020	3.2	3.058	.1202	.1221	98.4

3. EFFECTS OF SALTS AND OF OTHER REAGENTS UPON THE RATE OF FORMATION OF FURFURAL WHEN XYLOSE OR ARABINOSE IS STEAM-DISTILLED FROM 12 PERCENT HYDROCHLORIC ACID

Steam distillation of pentoses from 12 percent hydrochloric acid takes place at temperatures varying from 103° to 108° C. The addition of sufficient sodium chloride to saturate the acid solution increases

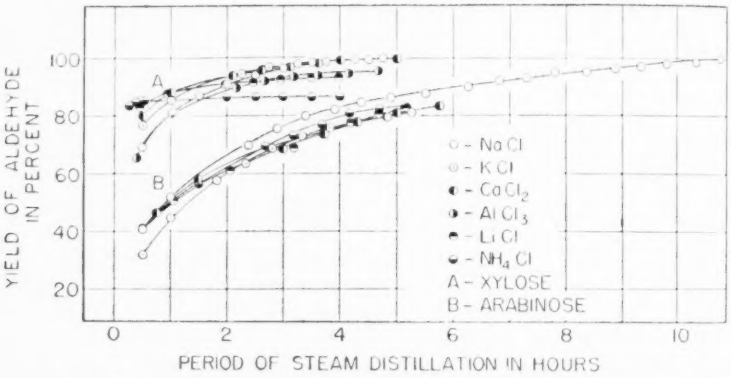

FIGURE 2.—*Effect of some salts upon the rate of formation of furfural when xylose or arabinose is steam-distilled in 12 percent hydrochloric acid.*

this temperature to 110° C. It was thought possible that salts which would give still higher temperatures would accelerate the formation of the furfural, which might be carried off by the steam before decomposition could take place. This would be especially desirable for the conversion of arabinose, which is much slower than that of xylose. For this purpose potassium, calcium, lithium, and ammonium chlorides were used. When it was found that no increases in yields were obtained in the first 2 liters of distillate, the distillations were not carried to completion.

The curves in figure 2 indicate that steam distillations from 12-percent solutions of hydrochloric acid containing sodium, potassium, or calcium chloride all give practically theoretical yields of furfural from xylose. Distillation takes place at 110° to 112° C, and the differences in the rates of formation of furfural are not significant. The use of lithium chloride with a higher temperature of distillation results in an increase in the initial rate of formation of furfural, but low yields are obtained. The first fraction of distillate is much more acid,

and this with the higher temperature favors polymerization, which probably accounts for the low yields of furfural. The addition of ammonium chloride causes the distillation to take place at 115° to 116° C, with the same resulting low yields. It has the added disadvantage that during steam distillation some material which reacts with bromine is obtained in the distillate. Steam distillations using 25 and 50 g of ammonium chloride in 12-percent hydrochloric acid produced material in 1 liter of distillate which consumed bromine corresponding to 0.4 ml and 0.8 ml of 0.1 *N* thiosulfate solution, respectively. A correction for this bromine consumption is necessary or false high values will be obtained. Stannous and zinc chlorides are distinctly disadvantageous, with yields of about 52 percent. A similar result was found by Kline and Acree [6] for stannous chloride.

TABLE 3.—*Effect of salts and other reagents upon the yields of furfural from xylose and arabinose*

Reagents added to 100 ml of 12-percent HCl	Approximate temperature of distilling solutions	Furfural obtained from 0.1 g of pentose	
		From xylose	From arabinose
A. STANDARD DISTILLATION. RATE OF 180 ml/hr			
	° *C.*	*Percent*	*Percent*
20 g of NaCl	110	88.2	73.4
50 g of $CaCl_2.2H_2O$	112	.....	72.5
50 g of NH_4Cl	115	.....	58.7
B. FAST STEAM DISTILLATION. RATE OF 400 ml/hr			
		Yield in 2 liters	Yield in total distillate
		Percent	*Percent*	*Percent*
20 g of NaCl	108 to 110	100.0	86.0	100.0
20 g of KCl	108 to 110	99.7	[a] 80.5	.....
25 g of $CaCl_2.2H_2O$	111 to 112	98.9	.....	.....
50 g of $CaCl_2.2H_2O$	111 to 112	99.7	83.0	[a] 95.0
20 g of LiCl	115 to 120	94.7	.....	.....
50 g of LiCl	115 to 126	.....	[a] 82.0	.....
30 g of $AlCl_3$	108 to 109	94.6	.....	.....
20 g of NH_4Cl	115 to 116	87.2 (corr.)	86.4 (corr.)	.....
50 g of NH_4Cl	115 to 116	86.2 (corr.)	.....	.....
36 g of $SnCl_2.2H_2O$	108 to 109	51.9	.....	.....
23 g of $ZnCl_2$	108 to 109	51.3	.....	.....
40 g of silica gel	103 to 108	94.9	.....	.....
20 g of silica gel and 30 g of KCl	109 to 110	100.5	80.5	100.1
20 g of NaCl and 0.02 g of iodine	110	.....	[a] 87.0 (corr.)	.....
20 g of NaCl and 0.07 g of piperidine	110	.....	[a] 70.5 (corr.)	.....
20 g of NaCl in 24-percent HCl	110	80.9	.....	.....

[a] Distillations were not carried to completion as indicated by the presence of furfural in the last fraction of distillate.

Although some of the salts appear better than others in the initial rate of conversion of xylose, the experiments show that the rate of conversion of arabinose is only slightly influenced by the different salts. The addition of very small amounts of iodine and piperidine, for which corrections also had to be made for bromine consumption by products in the distillate other than furfural, did not accelerate the rate of formation of furfural. The addition of silica gel instead of a soluble salt to give the effect of increased surface upon the rate of reaction without an increase in temperature offered no advantage.

When silica gel was used in conjunction with potassium chloride, there was no increase in rate of formation of furfural and practically the same yields were obtained as those found with potassium chloride alone.

As most of the determinations of the rate of production of furfural and methylfurfural required 10 or more steps in the titrations, it is not surprising that the final percentages show an error of 1 or 2 percent. Even though extreme caution was used to maintain a temperature of exactly 0° C for the titrations and a period of reaction with bromine of exactly 5 minutes, the uncertainty was greater in the determinations of methylfurfural than in the determinations of furfural.

The experiments show that the conversion of the smaller amounts of pentose is completed sooner than that of the larger quantities. For this reason, in applying this procedure, it is considered desirable to use amounts of pentose not in excess of 0.1 g.

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WASHINGTON, May 26, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1234

Part of Journal of Research of the National Bureau of Standards, Volume 23, August 1939

ELECTROPHORETIC STUDIES OF SILK

By Arnold M. Sookne and Milton Harris [1]

ABSTRACT

A microelectrophoretic technique was used to determine the characteristic pH-mobility curves for fibroin and for sericin and to ascertain the extent of removal of the latter during degumming by the soap and enzyme processes. The data suggest that sericin contains a much greater proportion of reactive groups than fibroin and indicate the importance of obtaining either uniform or complete removal of sericin during degumming processes.

The isoelectric points are shown to vary slightly with ionic strength. In acetate buffers of 0.02 *M* ionic strength, the isoelectric point of fibroin is 3.6 and that of sericin, 4.3.

Large ions of complex structure, such as phthalate or picrate, appear to have specific effects which are readily detectable by the electrophoretic technique.

Dissolved fibroin adsorbed on glass particles and fibroin regenerated from similar solutions had the same isoelectric points but different pH-mobility curves. Fibroin regenerated after dissolving in solutions of lithium bromide gave the same pH-mobility curve as untreated fibroin.

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I. INTRODUCTION

One of the principal difficulties involved in defining many of the characteristics of silk results from the fact that the naturally occurring fiber consists of at least two proteins, namely, silk fibroin and silk sericin, which have very different properties. Since the latter is generally removed from the fiber by empirical methods, the available data on many of the properties of the fibroin may be of questionable validity, especially since ordinary chemical methods are inadequate for determining the extent of removal of the sericin.

Sericin is a soluble protein which appears to form a coating on the surface of the fibroin. It has been shown by Abramson and others that a number of surfaces, when coated with any one of several proteins, assume electrophoretic properties similar to those of the ad-

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

sorbed materials; and it was felt, therefore, that an electrophoretic technique could be employed to advantage in studies of silk. Such an approach cannot only be used for studying the removal of sericin from fibroin but also has the additional advantage of contributing information relative to the amphoteric properties of the constituents of the naturally occurring fiber.

Electrophoretic techniques have been frequently used to investigate the properties of protein surfaces. Excellent discussions and reviews on the general subject have been presented by Abramson [1, 2],[2] and by Moyer [3].

One characteristic constant of a protein which is determined by its electrokinetic behavior is the isoelectric point. As defined by Abramson [1], the isoelectric state of a surface of a particle is that electrical state in which the sum of the positive and negative charges at the surface over a time average is equal to zero. The isoelectric point then is defined as the reference concentration of hydrogen ion or some other ion (Th^{++++}, for example) at which this condition is found. In other words, although it has become customary to define the isoelectric point in terms of the pH scale, it must be defined in terms which include a complete description of the medium in which no migration takes place. In the electrophoretic technique, the isoelectric point is, therefore, the point at which the electric mobility is zero.

It has been assumed by some investigators that the isoelectric state of a substance depends only on the state of its dissociable acid and basic groups (its combination with hydrogen or hydroxyl ions). Actually, however, it depends not only on the combination with hydrogen or hydroxyl ions but also with other anions or cations which may be in the solution.[3] The point at which dissociable groups of the substance combine equally and only with hydrogen and hydroxyl ions is defined as the *isoionic point* [4]. It should be noted that this is identical with the isoelectric point only when the substance does not combine with ions other than hydrogen or hydroxyl. It follows then, that while it may be possible to determine the isoelectric point by several methods (for example, by titration, provided the substance binds *only* H^+ or OH^-), electrophoresis is the only method by which the isoelectric point is determined in every case.

The most satisfactory results with electrophoretic techniques have been obtained with soluble proteins in solution or adsorbed on inert surfaces such as quartz, glass, or paraffin oil. In many cases it has been found that a protein adsorbed on such a surface has electrokinetic properties which are very similar to those obtained for the same protein when studied in the dissolved state or in the form of relatively insoluble particles. It has also been noted by Abramson that the titration and mobility curves are congruent for a number of soluble proteins, and by making certain assumptions, he has predicted the following: In solutions of the same ionic strength, the electric mobility of the same protein at different hydrogen-ion activities should be directly proportional to the number of hydrogen or hydroxyl ions bound by each molecule. In the case of some of the soluble proteins, the isoelectric and isoionic points have been found to be approximately the same.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] It should be noted that a surface may conceivably adsorb hydrogen or hydroxyl ions other than those bound by the acidic and basic groups.

Considerably more difficulty, however, is encountered in interpreting the results of investigations dealing with insoluble materials, especially those which are more or less crystalline in nature [5]. For example, in some materials of this type, the isoelectric and isoionic points have been found to be far apart. As a result, no attempt is made at this time to relate the data obtained to the specific acidic and basic properties of silk. However, it was found that the electrophoretic technique provided an excellent tool for distinguishing protein surfaces, and it was in this connection that it was used in the present investigation.

II. DESCRIPTION OF APPARATUS, METHODS, AND MATERIALS

An Abramson horizontal microelectrophoresis cell was employed in this investigation. The apparatus and methods were essentially the same as those described by Moyer [6]. The apparatus was checked from time to time by measuring the mobility of human erythrocytes in $M/15$ phosphate buffer at pH 7.4 [7]. A 28×ocular and 40×water-immersion objective were used for measurements involving soluble proteins adsorbed on glass particles. Particles of ground silk were observed with a 20×ocular and 20×objective.

In most cases, the mobilities were measured by observing the velocity during migration of the particles at the 0.21 and 0.79 depth levels of the cell, where the effect of the electroosmotic flow of the liquid is eliminated [6]. When the mobilities were very low, the velocities of the particles were measured in successive layers from the top to the bottom of the cell, and the mobility was evaluated by graphical integration of the curve obtained by plotting velocity against depth [1].

The majority of measurements were made on samples of raw and degummed silk which were reduced to a suitable particle size by cutting in a small, laboratory Wiley mill until the particles passed through a 60-mesh screen. A suspension of the particles in water was made and allowed to settle. The supernatant liquid was removed and found to contain particles approximately 1 to 5 microns in diameter.

The mobilities of dissolved silk or sericin were measured by adsorption of the protein on particles of Pyrex glass of 0.1 to 2 microns in diameter. The particles were thoroughly cleaned by washing with cleaning solution, water, concentrated hydrochloric acid, water, 0.001 N ammonium hydroxide, and then finally soaked for 3 days in distilled water, during which time the water was changed daily.

The mobilities of soluble materials were always measured in solutions containing a concentration of protein sufficient to insure complete coating of the glass particles. The required concentration was determined by measuring the mobility as a function of concentration of protein at constant pH and determining the point beyond which further increase in protein concentration caused no further change in the mobility of the glass particles.

All mobility measurements were made in a room at approximately 25° C. All values were corrected to 25° C by applying a factor of 2 percent per degree [6].

The pH values of the suspensions were measured with a MacInnes and Belcher type glass electrode and an electron ray meter. The pH values were referred to potassium acid phthalate (0.05 *M*) which was assigned a pH value of 4.01 [8].

The silk used was the product of the silkworm *Bombyx mori*.

III. EXPERIMENTAL

1. ELECTROPHORETIC PROPERTIES OF RAW SILK

Curve 1 in figure 1 shows the mobilities as a function of pH for three different samples of raw silk. The mobilities were measured after overnight immersion of the particles in hydrochloric acid–potassium chloride (pH range of 1.7 to 3.0) or acetic acid–sodium acetate (pH range of 3.0 to 6.5) solutions of ionic strength 0.02. Since

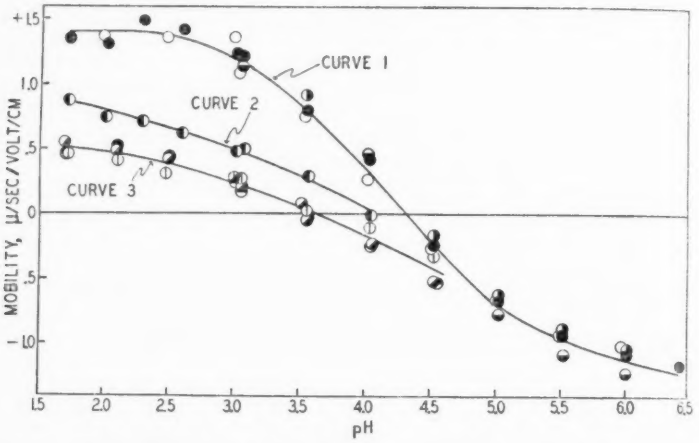

FIGURE 1.—*A comparison of the* pH-*mobility curves for raw and degummed silks.*

Curve 1 represents the mobilities for three different samples of raw silk, ●, ◒, ◑, and for sericin adsorbed on glass particles, ○. Curve 2 is that for silk degummed for 2 hours with soap. Curve 3 represents the results for 1, 2, and 3 cycles of degumming treatment as listed in the text.

sericin is relatively soluble, it was expected that some of the material would dissolve in this time and then completely coat the particles of cut-up silk. That curve 1 actually represents the mobility of sericin adsorbed on silk was demonstrated by the following experiments.

A sample of sericin was obtained by boiling 10 g of natural silk in two 150 ml portions of water for 15 minutes each. One drop of a suspension of Pyrex particles was then added to each of a series of solutions of the same pH but containing varying amounts of sericin. The mobilities of the glass particles were measured after allowing 15 minutes for adsorption. The two curves, shown in figure 2, were obtained by plotting mobility as a function of sericin concentration and indicate that complete coating of the glass particles by sericin occurs in solutions containing as little as 0.0001 percent of sericin. The mobility of sericin adsorbed on glass was then measured as a function of pH. The solutions used contained approximately 0.001 percent of the protein. The results as shown by the open circles in

curve 1, figure 1, indicate that the pH-mobility curve for the adsorbed sericin is identical with that obtained for the sericin on the silk fibers. The data also indicate that the sericin is isoelectric at pH 4.3.

2. ELECTROPHORETIC PROPERTIES OF DEGUMMED SILK

(a) SOAP DEGUMMING

Fifty grams of natural silk was boiled successively in four 2-liter portions of a 1-percent solution of soap for a total time of 2 hours, then extracted with cold alcohol and ether, and finally washed twice with water at 50° C. Curve 2 (fig. 1) is the pH-mobility curve for the degummed sample. After the above degumming treatment, some of

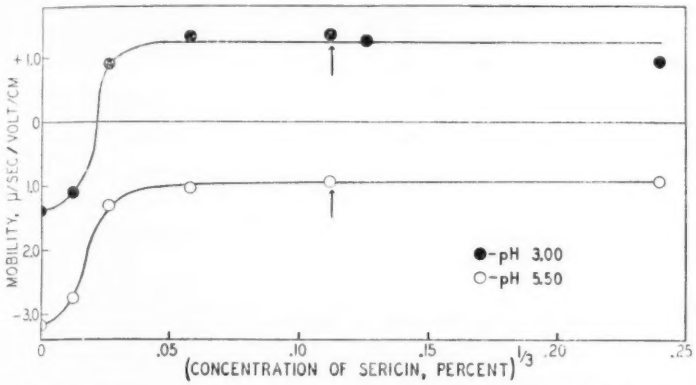

FIGURE 2.—*Mobility as a function of concentration of sericin at* pH *3.0 and* pH *5.5 in 0.02 M ionic strength buffers.*

the fibers were shaken with a hydrochloric acid–potassium chloride solution (ionic strength 0.02) of pH 1.77 containing some glass particles. It was found that an amount of sericin sufficient to alter the mobility of the glass particles was still present.

In an attempt to remove all of the sericin from the fibers, 10-g samples of the silk were subjected to successive cycles of the following treatments: a boil-off in 2-liter portions of a 1-percent solution of soap for three successive ½-hour periods, a 5-minute boil in 2 liters of water, a 5-minute rinse in 2 liters of 0.1 *N* ammonium hydroxide, a 5-minute rinse in 2 liters of 0.1 *N* hydrochloric acid, a 1-day wash in running distilled water, a 4-hour extraction with cold alcohol, and finally three successive rinses in distilled water at 50° C.

Curve 3, figure 1, shows results for samples subjected to one, two, and three cycles of the above series of treatments. No measurable change was produced after the first treatment, which appears to indicate that the samples were completely degummed. Curve 3 therefore represents the pH-mobility curve for fibroin and indicates that the material is isoelectric at pH 3.6 in 0.02-ionic-strength acetate buffers.

(b) ENZYME DEGUMMING

A 10-g sample of silk was treated with 1 liter of a solution containing 20 ml of Serizyme at 50° C for a total of about 500 hours. The enzyme solution was changed three times during the first 100

hours of treatment. Removal of sericin, as measured by loss in weight and nitrogen determinations, was rapid during the first 50 hours of treatment. The fibers continued to lose weight during the first 400 hours but appeared to reach a constant value after that time.

Figure 3 shows the results of pH-mobility measurements on the sample in hydrochloric acid–potassium chloride and acetic acid–sodium acetate solutions (ionic strength 0.005).[4]

Similar measurements, made at the same ionic strength on a sample of which had been completely degummed by the soap boil-off method, are included in the figure. The data obtained on the two samples are in good agreement and indicate the complete removal of the sericin.

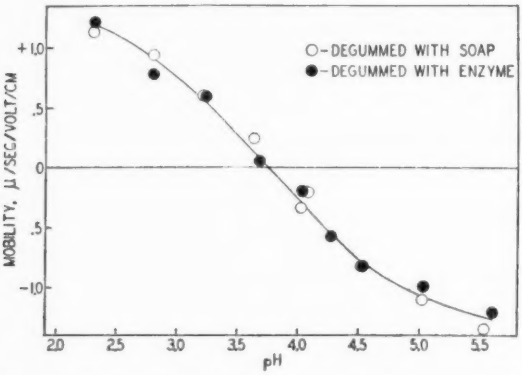

FIGURE 3.—*A comparison of* pH-*mobility curves for silk degummed by soap and enzyme treatments.*

3. EFFECT OF VARIATION OF IONIC STRENGTH

The curves in figure 4 represent data for soap-degummed fibroin in hydrochloric acid–potassium chloride buffers of 0.005, 0.02, and 0.05 ionic strength. The maximum shift in isoelectric point in these solutions is approximately 0.4 pH unit.

Figure 5 represents similar curves at 0.005 and 0.02 ionic strength for dissolved fibroin coated on glass particles. The material was prepared as follows: 0.5 g of degummed fibroin was heated in 5 ml of a 50-percent solution of lithium bromide (sp gr 1.53) on the steam bath for 5 minutes. The solution was dialyzed (specific resistance approximately 30,000 ohms), coated on glass particles, and the mobilities were measured. The curves show that the same relation between mobility and ionic strength holds for the dissolved fibroin as for the solid material.

4. SPECIFIC ION EFFECTS

The isoelectric points (3.5 to 3.9) obtained in the present investigation are higher than that (2.5) previously reported by Harris [9]. The differences appear to be too large to be accounted for by the differences in ionic strengths used in the two investigations. However, it was noted that hydrochloric acid–potassium acid phthalate buffers were used in the earlier investigations, which suggested that the differences might result from specific ion effects.

The effect of different ions in shifting the point of maximum flocculation and other protein characteristics has long been recognized [10, 11]. This is especially true for polyvalent ions [12]. Figure 6 shows the results of pH-mobility measurements in 6 different types of solutions on fibroin degummed by the soap boil-off method. All of the buffers except the phthalate were of ionic strength 0.02. The phthalate solutions varied in ionic strength from 0.05 to 0.10.

[4] The ionic strength was decreased from 0.02 used previously to 0.005 in order to facilitate measurements by increasing the mobilities.

Curve 2 represents the data obtained in the hydrochloric acid–potassium chloride, acetic acid–sodium acetate, and sulfuric acid–potassium sulfate solutions. In these systems the samples were isoelectric at about pH 3.6, although there may have been slight

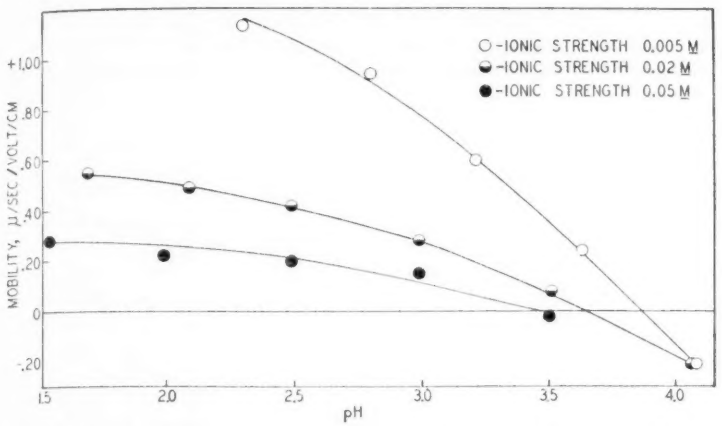

FIGURE 4.—*Effect of variation of ionic strength on the pH-mobility curve of degummed silk.*

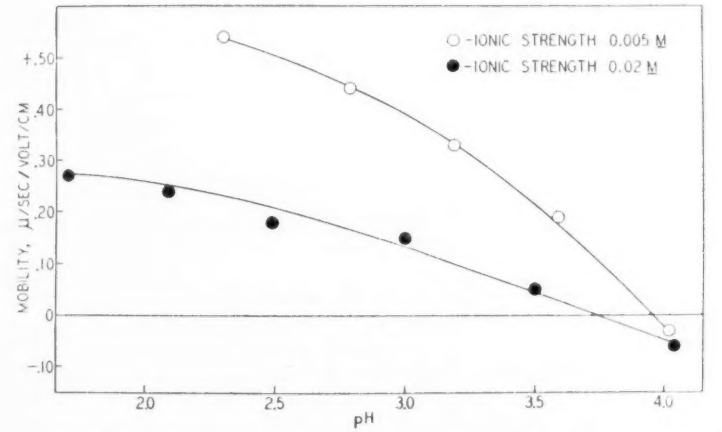

FIGURE 5.—*Effect of variation of ionic strength on the pH-mobility curve of dissolved fibroin adsorbed on glass particles.*

divergences between the different valence types. The phthalate buffers (curve 3) caused a shift in the isoelectric point of approximately 1 pH unit to pH 2.6, in agreement with the data of Harris.[5] Oxalic acid causes a smaller shift in the opposite direction (curve 1). In the picrate solutions (curve 4) the sample was so electronegative that it no longer exhibited an isoelectric point in the pH range used.

[5] The results for phthalate solutions (Clark's buffers) are not directly comparable with those for the other buffer types because of the difference in ionic strengths. However, the data given above for fibroin in solutions of different ionic strengths indicate that only a minor portion of the shift is caused by this factor. This is confirmed by the fact that a fivefold decrease in the ionic strengths of Clark's buffers causes an increase of only about 0.3 pH unit in the isoelectric point of wool [16].

5. EFFECT OF STATE OF AGGREGATION

Silk is readily dissolved by concentrated solutions of certain neutral salts [13, 14, 15]. With some salts, such as lithium bromide, solution is accomplished at room temperature.

A sample of degummed silk was dissolved by shaking with a 50-percent solution of lithium bromide at room temperature for several hours and the solution dialyzed against running distilled water. After about 2 days a precipitate was formed. Microscopic examina-

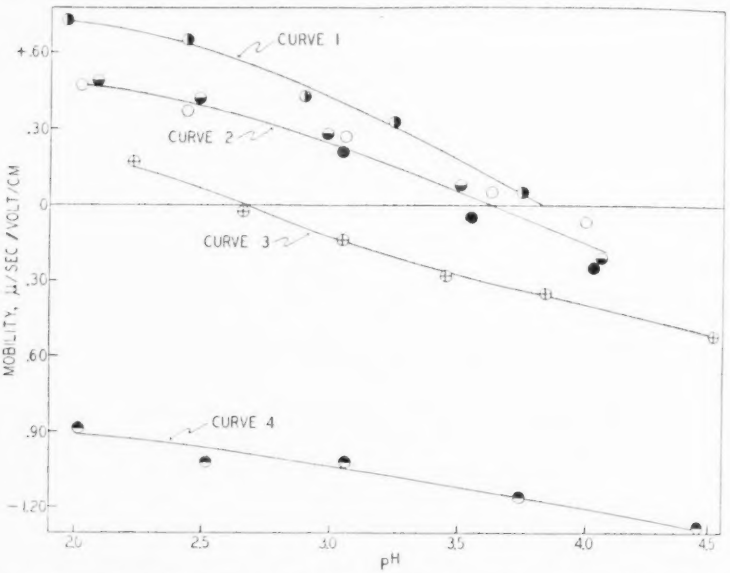

FIGURE 6.—*Effect of different ions on the electrophoretic mobility of degummed silk.*

Curve 1, oxalic acid-potassium hydroxide solutions. Curve 2, solutions of hydrochloric acid-potassium hydroxide, ◒; sulfuric acid-potassium hydroxide, ○; and acetic acid-sodium hydroxide, ●. Curve 3 Clark's phthalate buffers. Curve 4, picric acid-potassium hydroxide solutions.

tion of the material showed it to be made up of well-defined fibers which were strongly birefringent.

When the fibroin was dissolved by heating in a lithium bromide solution on a steam bath, spontaneous formation of a fibrous material did not occur during subsequent dialysis. On addition of ether, a precipitate which appeared to be somewhat fibrous and of low-order birefringence was obtained.

The pH-mobility curves in solutions of 0.005 *M* ionic strength for both samples of regenerated fibroin as well as for the dissolved materials coated on glass particles are given in figure 7.

IV. DISCUSSION

A comparison of the curve for sericin (curve 1, fig. 1) with that for fibroin (curve 3, fig. 1) shows that the mobility of the former is much greater, which strongly suggests that sericin contains a much greater proportion of the reactive carboxyl and basic amino groups. This has recently been confirmed by chemical analyses [16]. The practical significance is at once obvious. Many of the problems related to silk

and silk processing are in part, at least, concerned with the surface characteristics of the fiber. For example, the presence of a small amount of sericin may have a profound influence on the dyeing properties, and uneven distribution of the residual sericin would probably result in uneven dyeing of the fibers. It is not within the scope of the present investigation, however, to do more than point out some of the implications of these electrophoretic studies. The relationship of the difference in chemical properties between fibroin and sericin to the more practical aspects of silk chemistry is being studied separately [16].

The specific ion effects noted in figure 4 indicate that considerable care must be exercised in choosing buffer systems for protein investigations. These data also emphasize the necessity of including in the definition of the isoelectric point a description of the medium in which no migration takes place.

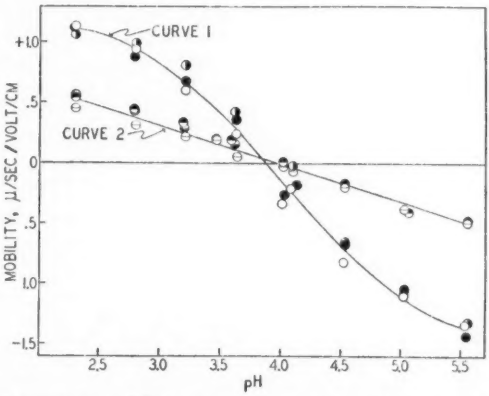

FIGURE 7.—*Effect of state of aggregation on the electrophoretic mobility of fibroin.*

Curve 1 represents the mobilities of degummed fibroin, ○; fibroin regenerated after solution in hot lithium bromide, ◑; and fibroin regenerated after solution in lithium bromide at room temperature, ●. Curve 2 is for dissolved fibroin adsorbed on glass. The solutions were obtained by heating fibroin in solutions of lithium bromide for 5 minutes, ◓, and for 2 hours, ◒, and by solution of fibroin at room temperature, ⊖.

Sufficient data are not available for the elucidation of the nature of specific ion effects. In general, it appears that the greatest anomalies arise when large ions of complex structure, such as phthalate or picrate, are used. The results suggest a number of possible explanations. For example, the acid of the buffer solution might react with basic groups of the fibroin to form a slightly ionized compound; the anion might react with or be adsorbed by the fiber in such a manner as to allow one of the acid groups of the adsorbed ion to be free; the strength of the acid or basic groups in the fiber might be altered by the proximity of the polar groups of the anion; or the adsorbed anion might provide charged centers which might even permit the adsorption of other ions.

It is well known that picric acid forms compounds with many proteins. Silk undoubtedly also forms picrates as evidenced by the color of the fibers. In the case of colorless ions such as phthalate ions, however, similar reactions are not at once obvious. The electrophoretic technique accordingly may often prove useful as a qualitative indication of such reactions.

Examination of the curves in figure 7 reveals a number of points of interest. The dissolved fibroin, adsorbed on glass particles (curve 2), exhibits lower mobilities than the untreated or regenerated fibroin (curve 1) throughout the pH range tested. The mobilities of the undissolved fibroin were roughly twice those of the dissolved material adsorbed either on glass or quartz particles. These data are in disagreement with earlier data by Harris [9] in which it appeared that the

mobilities were the same. The present work, however, indicates that the solutions used previously were too concentrated and, as a result, the majority of particles appearing in the solution were those of regenerated fibroin. These, as shown (solid and half-solid circles, curve 1), give a pH-mobility curve which is identical with that of untreated fibroin (open circles, curve 1).

Although only one curve is drawn to represent the points for the solid fibroin and one for the points for the dissolved material, it appears that dissolving fibroin in hot solutions may have produced slight alterations in it. For example, in curve 2, the points for the material obtained by solution at room temperature are consistently below those obtained for material dissolved in the hot solutions. The differences, however, are too small to warrant any further conclusions at this time.

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APPROXIMATION TO A FUNCTION OF ONE VARIABLE FROM A SET OF ITS MEAN VALUES

By Martin Greenspan

ABSTRACT

Physical data intended to represent the variation of a function of a single variable may be actually mean values of the function over intervals of the argument. Formulas for approximating to the values of the function from such data and examples of their use are presented in this paper. These formulas have been applied to problems of strain distribution in the Engineering Mechanics Section of the National Bureau of Standards.

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I. INTRODUCTION

Methods of measurement to determine the variation of a function with its argument are frequently such that only the mean values of the function over intervals of the argument are obtained. For example, a strain gage measures the total extension over the gage length and the mean strain is computed by dividing the extension by the gage length. If the variation of strain along the gage length is not nearly linear, the measured value may differ considerably from the strain at the middle of the gage length. This difference may be reduced by the use of a shorter gage length but as a result the sensitivity of the gage would be decreased and the gage would be more difficult to construct.

Another example is the measurement of heat capacity; the heat capacity, dQ/dt, of a body at temperature t is usually approximated by $\Delta Q/\Delta t$, where ΔQ is the quantity of heat required to change the temperature of the body by an amount Δt, where the interval Δt includes t.

A method of correcting such data was obtained by Strutt [1].[1] Strutt's formula is equivalent to the first correction-term of eq 12 in this paper. It will be seen that this is inadequate in many

[1] Figures in brackets indicate the literature references at the end of this paper.

cases. An analogous method for cases where the function is defined for discrete values of the argument only is King's formula for quinquennial sums [2].

Runge [3] has proposed a method of correcting observed spectral-energy distributions which has been applied by Stang [4], and by Runge to some data of Paschen. In this case the observed intensity is a double integral of the desired intensity, the error arising from the finite width of both the collimating slit and the bolometer strip. Runge's formula is not applicable to the problem considered here.

The statistical data which specify frequency distributions are often obtained in an approximate form analogous to the cases of strain and heat capacity. Thus, in a table of heights of individuals, the entry corresponding to 70 in. might be the number of individuals whose heights lie between 69½ and 70½ in. A method of computing the "true" moments of the distribution from the "rough" moments obtained from the data has been given by Sheppard [5]. Sheppard's work is the closest approach to a solution of the present problem found in the literature, but the method is in general not directly applicable.

II. DERIVATION OF THE FORMULAS

1. CENTRAL-DIFFERENCE FORMULA

Suppose that it is desired to determine the values of $f(x)$ corresponding to successive values of x differing by w, and that the method of measurement is such that the result, $F(x)$, is the average value of $f(x)$ over the interval g from $x-g/2$ to $x+g/2$. Then

$$F(x)=\frac{1}{kw}\int_{x-\frac{kw}{2}}^{x+\frac{kw}{2}} f(x)dx, \tag{1}$$

where $k=g/w$. This may be written symbolically as

$$F(x)=\frac{1}{kw}\delta_k\frac{f(x)}{D}, \tag{2}$$

where $D=d/dx$ and δ_k is defined from

$$\delta_k\psi(x)=\psi\left(x+\frac{kw}{2}\right)-\psi\left(x-\frac{kw}{2}\right). \tag{3}$$

Eq 1 may be written

$$f(x)=kw\frac{D}{\delta_k}F(x). \tag{4}$$

It is desired to calculate $f(x)$ in terms of $F(x)$ and its successive central differences, $\delta^n F(x)$, defined by repeated application of

$$\delta^n\psi(x)=\delta[\delta^{n-1}\psi(x)]$$

to eq 3 with $k=1$. The operators δ_k and D in eq 4 are thus to be replaced by equivalent expressions in terms of the operator δ. These

expressions are obtained by expanding the right-hand side of eq 3 in Taylor's series about x, thus:

$$\delta_k\psi(x)=e^{\frac{kw}{2}D}\psi(x)-e^{-\frac{kw}{2}D}\psi(x),$$

or

$$\delta_k=2\sinh\frac{kw}{2}D, \tag{5}$$

from which, with $k=1$,

$$D=\frac{2}{w}\sinh^{-1}\frac{\delta}{2}. \tag{6}$$

The substitution of D from eq 6 into eq 5 gives

$$\delta_k=2\sinh\left(k\sinh^{-1}\frac{\delta}{2}\right). \tag{7}$$

Replacement of D and δ_k in eq 4 by the values given in eq 6 and 7 gives

$$f(x)=\frac{k\sinh^{-1}\frac{\delta}{2}}{\sinh\left(k\sinh^{-1}\frac{\delta}{2}\right)}F(x). \tag{8}$$

This is in the form $f(x)=p\,\mathrm{csch}\,p\,F(x)$, where $p=k\sinh^{-1}(\delta/2)$, and by expansion of p csch p in Maclaurin's series may be written

$$f(x)=\left[1+2\sum_{n=1}^{\infty}\frac{(-1)^n(2^{2n-1}-1)}{(2n)!}B_{2n-1}\left(k\sinh^{-1}\frac{\delta}{2}\right)^{2n}\right]F(x), \tag{9}$$

where B_{2n-1} are the successive Bernoulli's numbers.[2] Expansion of $\sinh^{-1}(\delta/2)$ in Maclaurin's series in eq 9 gives the double series

$$f(x)=\left\{1+2\sum_{n=1}^{\infty}(-1)^n\frac{(2^{2n-1}-1)}{(2n)!}B_{2n-1}\left[\frac{k\delta}{2}\left(1+\sum_{m=1}^{\infty}(-1)^m\frac{(2m)!}{(2^m m!)^2(2m+1)}(\delta/2)^{2m}\right)\right]^{2n}\right\}F(x), \tag{10}$$

or

$$f(x)=\left[1-\frac{k^2}{24}\delta^2+\frac{k^2(20+7k^2)}{5760}\delta^4-\frac{k^2(448+196k^2+31k^4)}{967{,}680}\delta^6+\ldots\right]F(x). \tag{11}$$

When $k=1$, which is the case when the intervals g are contiguous, eq 11 reduces to

$$f(x)=\left(1-\frac{1}{24}\delta^2+\frac{3}{640}\delta^4-\frac{5}{7168}\delta^6+\ldots\right)F(x). \tag{12}$$

The numerical values of the coefficients of the first three correction terms in eq 11 are given for four values of k, in table 1.

[2] What are here denoted by B_{2n-1} are sometimes denoted by B_n.

TABLE 1.—*Values of* C_2, C_4, *and* C_6 *in* $f(x)=(1+C_2\delta^2+C_4\delta^4+C_6\delta^6+\ldots)\,F(x)$

k	$-C_2$	C_4	$-C_6$	k	$-C_2$	C_4	$-C_6$
1	0.0417	0.00469	0.000714	3	0.375	0.130	0.043
2	.167	.0333	.00714	4	.667	.367	.191

2. DESCENDING-DIFFERENCE FORMULA

Equations 11 and 12 cannot be used to calculate $f(x)$ at $x=b$, where b is near a boundary of the interval of x for which $f(x)$ is defined, or where values of x on only one side of b are accessible to the method of measurement, because the necessary central differences are not available. For such cases an ascending- or descending-difference formula may be used. It is convenient to consider the measured value $F(x)$ to correspond to the initial point of the interval $g=kw$, so that

$$F(x)=\frac{1}{kw}\int_x^{x+kw} f(x)dx, \tag{13}$$

or, symbolically,

$$F(x)=\frac{1}{kw}\Delta_k\frac{f(x)}{D}, \tag{14}$$

where $D=d/dx$ and Δ_k, the descending difference, is defined from

$$\Delta_k\psi(x)=\psi(x+kw)-\psi(x). \tag{15}$$

Equation 14 may be written

$$f(x)=kw\frac{D}{\Delta_k}F(x). \tag{16}$$

It is desired to calculate $f(x)$ in terms of $F(x)$ and its successive descending differences $\Delta^n F(x)$, defined by repeated application of

$$\Delta^n\psi(x)=\Delta[\Delta^{n-1}\psi(x)]$$

to eq 15 with $k=1$. The operators Δ_k and D in eq 16 are thus to be replaced by equivalent expressions in terms of the operator Δ. Equation 15 may be written

$$(1+\Delta_k)\psi(x)=\psi(x+kw)=e^{kwD}\psi(x),$$

or

$$1+\Delta_k=e^{kwD}, \tag{17}$$

and

$$1+\Delta=e^{wD}. \tag{18}$$

Equation 17 and 18 give

$$wD=\log\,(1+\Delta), \tag{19}$$

and

$$\Delta_k=(1+\Delta)^k-1. \tag{20}$$

Replacement of D and Δ_k in eq 16 by the values given in eq 19 and 20 gives

$$f(x)=\frac{\log\ (1+\Delta)^k}{(1+\Delta)^k-1}F(x). \tag{21}$$

This is in the form $f(x)=\frac{p}{e^p-1}F(x)$, where $p=k\ \log\ (1+\Delta)$, and by expansion of $p/(e^p-1)$ in Maclaurin's series may be written

$$f(x)=\left\{1-\frac{k}{2}\log\ (1+\Delta)+\sum_{n=1}^{\infty}\frac{(-1)^{n+1}B_{2n-1}}{(2n)!}[k\ \log\ (1+\Delta)]^{2n}\right\}F(x), \tag{22}$$

where B_{2n-1} are the successive Bernoulli's numbers.[3] Expansion of $\log\ (1+\Delta)$ in Taylor's series in eq 22 gives the double series

$$f(x)=\left\{1-\frac{k}{2}\sum_{m=1}^{\infty}(-1)^{m+1}\frac{\Delta^m}{m}+\sum_{n=1}^{\infty}\frac{(-1)^{n+1}B_{2n-1}}{(2n)!}k^{2n}\left[\sum_{m=1}^{\infty}(-1)^{m+1}\frac{\Delta^m}{m}\right]^{2n}\right\}F(x),$$

or (23)

$$f(x)=\left[1-\frac{k}{2}\Delta+\frac{k}{4}\left(1+\frac{k}{3}\right)\Delta^2-\frac{k}{6}\left(1+\frac{k}{2}\right)\Delta^3+\frac{k}{8}\left(1+\frac{11k}{18}-\frac{k^3}{90}\right)\Delta^4\right.$$
$$\left.-\frac{k}{2}\left(\frac{1}{5}+\frac{5k}{36}-\frac{k^3}{180}\right)\Delta^5+\frac{k}{12}\left(1+\frac{137k}{180}-\frac{17k^3}{360}+\frac{k^5}{2520}\right)\Delta^6+\ .\ .\ .\right]F(x). \tag{24}$$

When $k=1$, which is the case when the intervals g are contiguous, eq 24 reduces to

$$f(x)=\left(1-\frac{1}{2}\Delta+\frac{1}{3}\Delta^2-\frac{1}{4}\Delta^3+\frac{1}{5}\Delta^4-\frac{1}{6}\Delta^5+\frac{1}{7}\Delta^6-\ .\ .\ .+\ .\ .\ .\right)F(x). \tag{25}$$

The numerical values of the coefficients of the first six correction terms in eq 24 are given, for four values of k, in table 2.

TABLE 2.—*Values of* C_1, C_2, *etc. in* $f(x)=(1+C_1\Delta+C_2\Delta^2+C_3\Delta^3+\ .\ .\ .)F(x)$

k	$-C_1$	C_2	$-C_3$	C_4	$-C_5$	C_6
1	0.500	0.333	0.250	0.200	0.167	0.143
2	1.000	.834	.667	.533	.433	.360
3	1.500	1.500	1.250	.950	.700	.526
4	2.000	2.333	2.000	1.367	.800	.476

III. ACCURACY AND LIMITATIONS

The derivations of eq 11 and 24 involve the expansion of operators in terms of ascending powers (orders) of the symbols δ and Δ, respectively. This procedure is strictly valid if the function $F(x)$ upon which the expanded expression operates is a polynomial, because δ and Δ obey the commutative, associative, and distributive laws; and because, since the operation δ or Δ on a polynomial of finite degree n reduces its degree by one, all differences of $F(x)$ of order higher than the nth vanish. The series therefore terminates, and is exact.

However, if $F(x)$ is not a polynomial, the formulas 11 and 24 can be applied only on the assumption that $F(x)$ may be sufficiently well represented by a polynomial of degree n. The error involved in such a procedure might be estimated by considering the remainder after

[3] See footnote 2.

the nth difference term of the series, but this is not possible when, as is usually the case, the characteristics of $F(x)$ are unknown. The justification for the use of formulas 11 and 24 therefore rests on the fact that distributions encountered in practice are frequently such that they may be approximated to by polynomials of low degree.

It is obvious that, so far as the data $F(x)$ are concerned, the function $f(x)$ is undetermined to the extent of an additive arbitrary periodic function of period g the average value of which over any interval g is zero. This indetermination can be reduced only by reducing the interval g over which $f(x)$ is averaged in the measurement. Of course, a lower limit to g is set by other considerations.

The value for the interval w between observations may ordinarily be the same as that which would for various reasons have been used if the corrections were not to be applied. In cases where there are not enough data to provide differences of sufficiently high order, w can be decreased. The highest order of differences which can be advantageously used is determined by the accuracy of the data. The successive differences are increasingly affected by the errors of measurement, and the differences of a certain order, and all succeeding differences, will consist mostly of accumulated error. It may be desirable to graduate the data $F(x)$ before applying eq 11 or 24.

IV. EXAMPLES

It was thought desirable to include the following two examples which indicate roughly the order of accuracy to be expected from the use of eq 11 and 24. For these examples hypothetical data were obtained by computing mean values of strain over intervals of length g from theoretically known strain distributions. These mean values represent data that would be obtained by a perfect strain gage of gage length g.

1. CENTRAL-DIFFERENCE FORMULA

Consider (fig. 1) a very long isotropic elastic strip of breadth $2b$ containing a centrally located circular hole of diameter b. The strip is in a state of generalized plane stress such that the stress at cross sections remote from the hole is of magnitude $\widehat{xx} \rightarrow T$, uniform across the section and normal to it. The boundaries of the strip are free. The curve of figure 1 shows according to Howland [6] the variation of stress along an edge of the strip near the hole. Suppose that in a certain specimen the stresses along an edge were actually as given by the curve of figure 1 and it were desired to determine them by means of a strain gage. (Since the edge of the strip is a free boundary, the stress is proportional to the strain.) The data that would be obtained by the use of a strain gage of gage length $(2/3)b$ and the results of applying eq 11 are shown in figure 1. It is evident that the corrected values conform much more closely than the data to the original distribution.

2. DESCENDING-DIFFERENCE FORMULA

Consider (fig. 2) an isotropic elastic flat circular plate of radius a and thickness $h \ll a$, clamped around the edge and subjected to a hydrostatic pressure $p = 18.8E(h^4/a^4)$ on one face. (E is Young's modulus of elasticity and Poisson's ratio is taken as 1/4.) The curve of figure 2 shows according to Nádai [7] the variation along a radius of

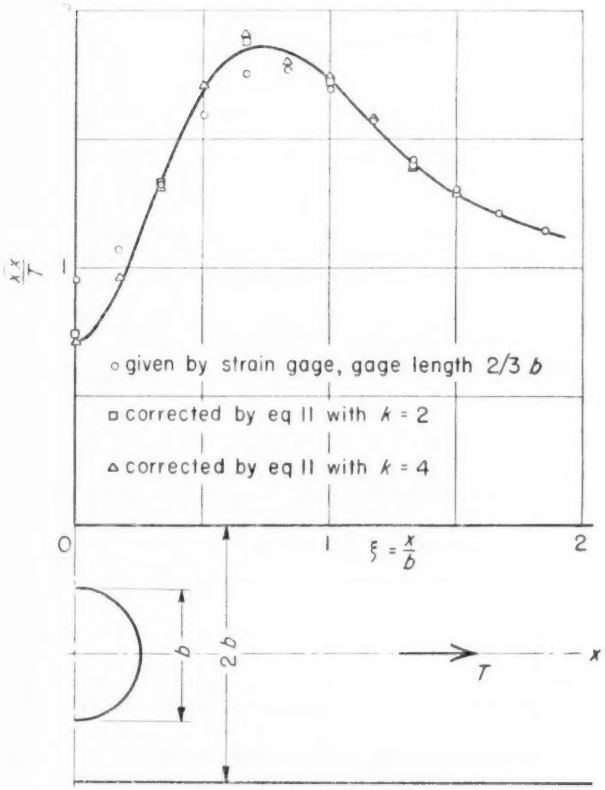

FIGURE 1.—*Problem of a tension member containing a hole.*

$\epsilon_r \Big/ \frac{h^2}{12a^2}$, where ϵ_r is the normal strain in the unloaded face in the radial direction. Suppose that in a certain specimen the radial strains were actually as given by the curve of figure 2 and it were desired to determine them by means of a strain gage. If the value of the strain at the clamped edge were desired, eq 24 would be used with the transformation $x=1-u$. The data that would be obtained by the use of strain gages of gage lengths $(2/5)a$ and $(4/5)a$ and the results of applying eq 24 are shown in figure 2.

The corrected values conform much more closely than the data to the original distribution. Furthermore, the value of $\epsilon_r \Big/ \frac{h^2}{12a^2}$ at the clamped edge, which is inaccessible to the strain gage, is accurately obtained.

3. NOTATION

Various notations for differences are in use. Tables 3 and 4 show how the differences used in this paper are computed. The tables are arranged so that the difference corresponding to any entry, $F(x)$, is on a horizontal line through that entry.

The interval between successive values of the argument x is constant.

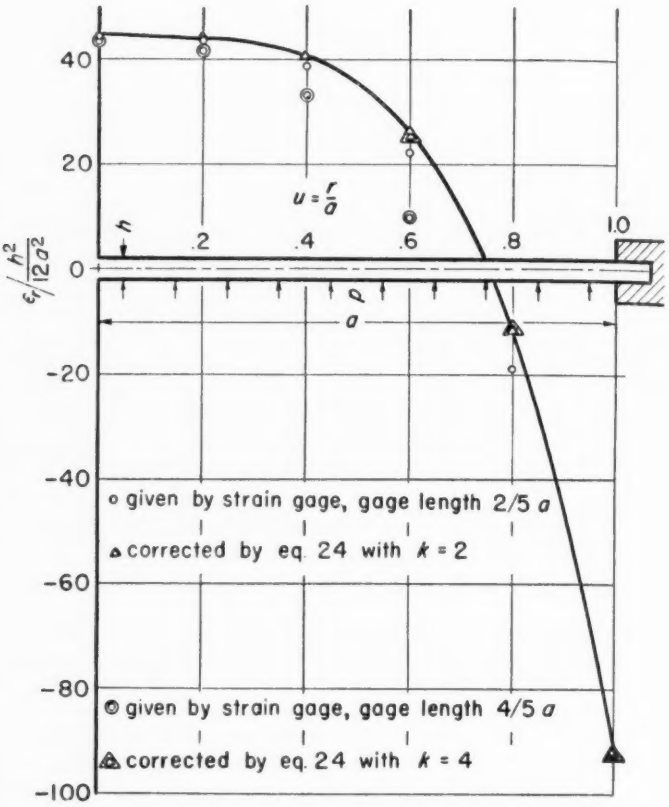

FIGURE 2.—*Problem of a circular flat plate subjected to hydrostatic pressure.*

TABLE 3.—*Central differences*

$F(x)$	$\delta F(x)$	$\delta^2 F(x)$	$\delta^3 F(x)$	$\delta^4 F(x)$
$F(x_0)$				
	$\delta F(x_{1/2}) = F(x_1) - F(x_0)$			
$F(x_1)$		$\delta^2 F(x_1) = \delta F(x_{3/2}) - \delta F(x_{1/2})$		
	$\delta F(x_{3/2}) = F(x_2) - F(x_1)$		$\delta^3 F(x_{3/2}) = \delta^2 F(x_2) - \delta^2 F(x_1)$	
$F(x_2)$		$\delta^2 F(x_2) = \delta F(x_{5/2}) - \delta F(x_{3/2})$		$\delta^4 F(x_2) = \delta^3 F(x_{5/2}) - \delta^3 F(x_{3/2})$
	$\delta F(x_{5/2}) = F(x_3) - F(x_2)$		$\delta^3 F(x_{5/2}) = \delta^2 F(x_3) - \delta^2 F(x_2)$	
$F(x_3)$		$\delta^2 F(x_3) = \delta F(x_{7/2}) - \delta F(x_{5/2})$		$\delta^4 F(x_3) = \delta^3 F(x_{7/2}) - \delta^3 F(x_{5/2})$
	$\delta F(x_{7/2}) = F(x_4) - F(x_3)$		$\delta^3 F(x_{7/2}) = \delta^2 F(x_4) - \delta^2 F(x_3)$	
$F(x_4)$		$\delta^2 F(x_4) = \delta F(x_{9/2}) - \delta F(x_{7/2})$		$\delta^4 F(x_4) = \delta^3 F(x_{9/2}) - \delta^3 F(x_{7/2})$
	$\delta F(x_{9/2}) = F(x_5) - F(x_4)$		$\delta^3 F(x_{9/2}) = \delta^2 F(x_5) - \delta^2 F(x_4)$	
$F(x_5)$		$\delta^2 F(x_5) = \delta F(x_{11/2}) - \delta F(x_{9/2})$		$\delta^4 F(x_5) = \delta^3 F(x_{11/2}) - \delta^3 F(x_{9/2})$
	$\delta F(x_{11/2}) = F(x_6) - F(x_5)$		$\delta^3 F(x_{11/2}) = \delta^2 F(x_6) - \delta^2 F(x_5)$	
$F(x_6)$		$\delta^2 F(x_6) = \delta F(x_{13/2}) - \delta F(x_{11/2})$		
	$\delta F(x_{13/2}) = F(x_7) - F(x_6)$			
$F(x_7)$				

TABLE 4.—*Descending differences*

$F(x)$	$\Delta F(x)$	$\Delta^2 F(x)$	$\Delta^3 F(x)$	$\Delta^4 F(x)$
$F(x_0)$	$\Delta F(x_0)=F(x_1)-F(x_0)$	$\Delta^2 F(x_0)=\Delta F(x_1)-\Delta F(x_0)$	$\Delta^3 F(x_0)=\Delta^2 F(x_1)-\Delta^2 F(x_0)$	$\Delta^4 F(x_0)=\Delta^3 F(x_1)-\Delta^3 F(x_0)$
$F(x_1)$	$\Delta F(x_1)=F(x_2)-F(x_1)$	$\Delta^2 F(x_1)=\Delta F(x_2)-\Delta F(x_1)$	$\Delta^3 F(x_1)=\Delta^2 F(x_2)-\Delta^2 F(x_1)$	$\Delta^4 F(x_1)=\Delta^3 F(x_2)-\Delta^3 F(x_1)$
$F(x_2)$	$\Delta F(x_2)=F(x_3)-F(x_2)$	$\Delta^2 F(x_2)=\Delta F(x_3)-\Delta F(x_2)$	$\Delta^3 F(x_2)=\Delta^2 F(x_3)-\Delta^2 F(x_2)$	$\Delta^4 F(x_2)=\Delta^3 F(x_3)-\Delta^3 F(x_2)$
$F(x_3)$	$\Delta F(x_3)=F(x_4)-F(x_3)$	$\Delta^2 F(x_3)=\Delta F(x_4)-\Delta F(x_3)$	$\Delta^3 F(x_3)=\Delta^2 F(x_4)-\Delta^2 F(x_3)$	$\Delta^4 F(x_3)=\Delta^3 F(x_4)-\Delta^3 F(x_3)$
$F(x_4)$	$\Delta F(x_4)=F(x_5)-F(x_4)$	$\Delta^2 F(x_4)=\Delta F(x_5)-\Delta F(x_4)$	$\Delta^3 F(x_4)=\Delta^2 F(x_5)-\Delta^2 F(x_4)$	
$F(x_5)$	$\Delta F(x_5)=F(x_6)-F(x_5)$	$\Delta^2 F(x_5)=\Delta F(x_6)-\Delta F(x_5)$		
$F(x_6)$	$\Delta F(x_6)=F(x_7)-F(x_6)$			
$F(x_7)$				

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PREPARATION OF CRUCIBLES FROM SPECIAL REFRACTORIES BY SLIP-CASTING

By John G. Thompson and Manley W. Mallett

ABSTRACT

The slip-casting process, which is widely used in ceramics, has not been generally applied to the preparation of crucibles from special refractories, which lack the property of plasticity. However, enough plasticity to make slip-casting feasible can be developed in some of the special refractories by fine grinding and treatment with acid. Thin-walled crucibles of alumina, beryllia, zircon, zirconia, and electrically fused thoria were cast from aqueous slips, and bricks 5 cm thick were made by a modified process. Magnesia crucibles could not be cast from aqueous slips but were formed successfully from a suspension of finely ground magnesia in absolute alcohol.

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I. INTRODUCTION

Researches in refractory materials frequently are necessitated by metallurgical researches at elevated temperatures, particularly when treatment of molten metal of high purity is involved. The material from which crucibles are made must be chemically inert to the molten metal, free from impurities that may be transferred to the metal, and must not melt or soften in use. The containers for this type of research must be of the desired shape, size, and capacity, sufficiently strong and resistant to thermal and mechanical shock, and resistant to the erosive action of the molten metal.

Except for carbon or graphite, which react with many metals at elevated temperatures, refractory materials with melting points above 1,600° C, and of sufficiently high purity and chemical stability to be suitable for melting high-purity metals, practically are limited to purified oxides (and in some cases silicates), such as those of aluminum, beryllium, calcium, magnesium, thorium, and zirconium. The relative merits of these refractory materials and the factors that determined the selection of one or another in several investigations at the National Bureau of Standards, have been discussed in previous publications [1, 2, 3, 4].[1] Crucibles were formed by tamping or pressing the refractory into the desired shape, as described in detail by Swanger and Caldwell [3].

[1] Figures in brackets indicate the literature references at the end of this paper.

Crucibles prepared in this manner have been quite satisfactory for small melts of highly purified metals, particularly metals of the platinum group and their alloys. However, in the current study of high-purity iron [4] it became evident that the pressing or tamping procedure was not so satisfactory for the production of larger crucibles for melting 600 to 800 g of iron. The preparation of these relatively thick-walled crucibles required large amounts of refractory, and their bulk was objectionable in a furnace whose capacity was limited. However, the principal objection to tamped crucibles, for melting high-purity iron in a high-frequency induction furnace, was contamination of the melt by particles detached from the walls of the crucible. Ingots of iron melted and allowed to solidify in tamped crucibles usually had very rough surfaces in which large and small particles of refractory were tightly embedded, and even the apparently clean metal from the interior of the ingots was contaminated to some extent by the refractory, as was shown by the results of spectroscopic examination.

Attention was therefore turned to other methods of preparing crucibles, primarily to obtain more resistant and more nearly perfect inner surfaces. It was found that the process of slip-casting, which is so widely used in the ceramic industry, could be modified to produce high-quality, thin-walled crucibles of the desired type from nonplastic refractory materials.

The process of slip-casting, as applied to the production of clay ware, is simple in principle. The "slip," which is an aqueous suspension of the clay mixture, is poured into a plaster of paris mold where it gradually solidifies by absorption by the plaster of water from the slip. The solidified casting is subsequently removed from the mold and is dried and fired.

Although the slip-casting process for the production of clay ware is simple in principle, its successful application requires control of many variables, which were discussed in detail by Hall [5].

Slip-casting of special refractories differs from that of clay in one important respect, that is, most clays are more or less plastic and self-bonding, whereas the special refractories are nonplastic. This is particularly true of calcined refractories; and calcination, to preshrink the material prior to forming it into crucibles for use at high temperatures, is quite necessary to minimize destructive shrinkage of the completed crucible when it is fired. In earlier work on the slip-casting of special refractories at this Bureau [1], small amounts of clay or organic compounds were incorporated in the slip to serve as a bond for the nonplastic refractory, but this practice was not entirely satisfactory because the added material lowered the softening temperature of the refractory, or because it contaminated the high-purity metal in subsequent melting operations, or both. However, Ruff [6] showed that the addition of a plastic material was not always necessary, and that treatment of finely ground refractory oxides with acids or alkalies developed plasticity in the otherwise nonplastic materials. Ruff worked with zirconia, alumina, and silica. Our study of slip-casting started with beryllia, which was the refractory selected for the work with high-purity iron, and was extended to include other refractories.

II. SLIP-CAST BERYLLIA CRUCIBLES

The beryllia used in this work was a commercial product of "chemically pure" grade prepared by calcination of beryllium sulphate. The beryllia was heated to about 1,800° C in graphite shells in an evacuated Arsem furnace to convert the finely granulated powder to a loosely coherent cake whose volume was approximately 85 percent of that of the powder. The cake, after being crushed to pass through a No. 10 sieve, was ground in a steel ball mill which was two-thirds filled with a mixture of equal volumes of beryllia and steel balls 1 inch in diameter. The mill rotated at about 70 rpm. Satisfactory grinding was determined by the behavior of the material in casting operations rather than by direct determinations of the particle sizes. Insufficient grinding was indicated by the presence of coarse particles which settled rapidly from the casting slip, and by a rough, sandy surface and low strength in the castings. Over-ground material yielded castings that formed very slowly and that cracked in drying. It was found that 8 hours' grinding yielded satisfactory material, and this grinding period was used in all of the work with beryllia. Wet grinding appeared to be somewhat faster than dry grinding, but the latter was generally used in our work because of greater convenience in cleaning the dry mill and in storing the dry powder.

Enough of the ground material to produce 1 day's castings was transferred to a large bottle together with about twice its volume of diluted hydrochloric acid (1+9), and the mixture was thoroughly shaken. Reaction of the acid with fine particles of iron from the ball mill kept the mixture stirred at first; but when the mixture stood for 2 or 3 hours, the beryllia settled out and most of the discolored acid could be removed by siphoning. Fresh acid was added and was mixed with the beryllia by shaking. After a suitable period of settling, the spent acid was replaced by a third portion of fresh acid, the mixture was shaken and then allowed to stand overnight, after which the supernatant acid was siphoned off as completely as possible.

This treatment was sufficient to impart the necessary plasticity to the beryllia and to remove the iron which was introduced during grinding. Good crucibles could be prepared from a suspension of the acid-washed beryllia in diluted hydrochloric acid, but equally good castings could be obtained from less-acid slips which were less destructive to the plaster molds. Consequently, after siphoning off the final portion of diluted acid, the beryllia was washed three or four times with water. The beryllia settled more slowly with each successive washing until, after the final addition of fresh water, the supernatant liquid remained cloudy for several hours. After the mixture had stood overnight, the water was siphoned off as completely as possible. This left the beryllia in the form of a firm, damp cake which could be transformed, by stirring or shaking, into a thinly fluid slip. Too much dilution caused rapid settling of the slip, whereas an insufficient amount of water produced a viscous slip from which it was difficult to eliminate air bubbles. If the consistency of the slip was that of rather thin cream and, further, if the entrapped air bubbles rose rapidly and freely to the surface before appreciable settling of the beryllia occurred, the slip was ready for casting. A few observations of the volumes of diluted acid and water that were added to and siphoned from the beryllia showed that satisfactory slips usually contained between 60 and 70 percent by weight of solid matter.

To form a crucible, the slip was poured into the plaster mold[2] rapidly but without splashing or entrapping air. The plaster immediately began to absorb water from the slip, and a film of solidified material formed on the walls. The liquid level within the mold was maintained by additions of slip until the film of solidified material reached the desired thickness. The mold was then inverted and the residual liquid slip was poured out. The time required to form a crucible with a wall thickness of 2 or 3 mm usually was about 1 minute, but this varied with the consistency and acidity of the slip and with the condition of the plaster mold. If the plaster was too wet, the crucible formed slowly, hardened slowly, and adhered to the mold. Similar difficulties were encountered in casting an old slip in which the beryllia had been wet continuously with acid or water for more than a week. If the plaster was too dry, the crucible formed so rapidly that the process was hard to control, and the crucible usually collapsed and was poured out of the mold along with the excess of liquid slip. When the proper condition of a plaster mold was once attained, it could be maintained by making only one or two castings per day, then inverting the empty mold and allowing it to dry overnight. With this schedule 25 or more crucibles have been cast in a single mold, although the later crucibles in the sequence formed slowly because of slow absorption by the old plaster, and these crucibles were removed with difficulty from the mold because rough spots in the plaster served to anchor the crucible to the mold. Some molds reached the limit of their usefulness when they began to produce bubbles of gas, either because of some chemical reaction, such as that of hydrochloric acid with calcium carbonate, or because there were channels in the plaster from which the air was displaced by the water absorbed during a casting. Such gas bubbles were retained in the semisolidified slip and produced imperfect crucibles.

If the crucible formed properly, it remained in the mold when the excess of liquid slip was poured out; but it was too soft and plastic at this stage to support its own weight or to be removed from the mold. The crucible, therefore, was allowed to remain in the mold for further drying by absorption of water by the plaster and by evaporation from the inner surface of the casting. After about 2 hours the inner surface was dry and firm to the touch and shrinkage cracks began to appear at the junction of the top of the crucible and the wall of the mold. The casting then could be removed from the mold, particularly if the mold was gently tapped and rolled before it was inverted. The crucibles at this stage were somewhat plastic but were strong enough to be removed from the mold without collapsing. They were air-dried for about 24 hours and then were heated slowly for another 24 hours during which the temperature rose to about 180° C. Drying in this manner did not appreciably affect the dimensions of the crucible, but subsequent firing to 1,750° or 1,800° C was accompanied by a linear shrinkage of about 10 percent. The density and shrinkage of the crucible increased, and the porosity decreased,

[2] The molds in which the castings were made were prepared as follows: Plaster of Paris of a grade suitable for making molds was stirred into water in the approximate proportions of 4 parts by weight of plaster to 3 parts of water. The thoroughly mixed mass was gently stirred and jarred to eliminate air bubbles and was then poured into a cardboard cylinder in which was suspended a slightly tapered brass mandrel that was covered with a thin film of lard oil. The mandrel and cylinder were arranged to produce a plaster casting with uniform thickness (about 3 cm) of walls and bottom. The inner surface of a satisfactory plaster casting, after the mandrel was withdrawn, was smooth and free from gas pockets or mechanical defects. The cardboard shell was stripped from the solidified plaster, and after the mold had been allowed to air-dry for several days at room temperature, it was ready for use.

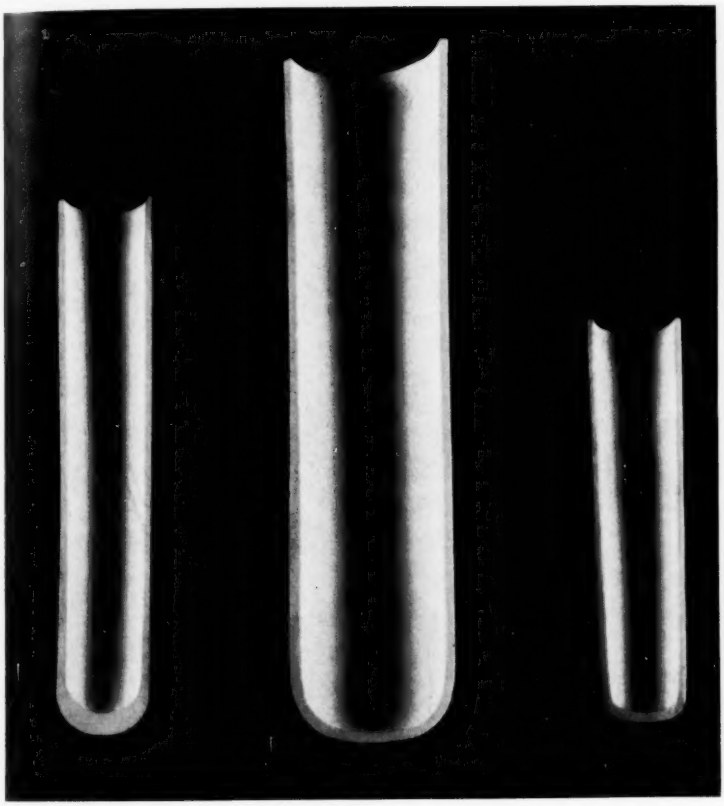

FIGURE 1.—*Sections of slip-cast crucibles, exhibiting the smooth inner surfaces and thin uniform walls.*

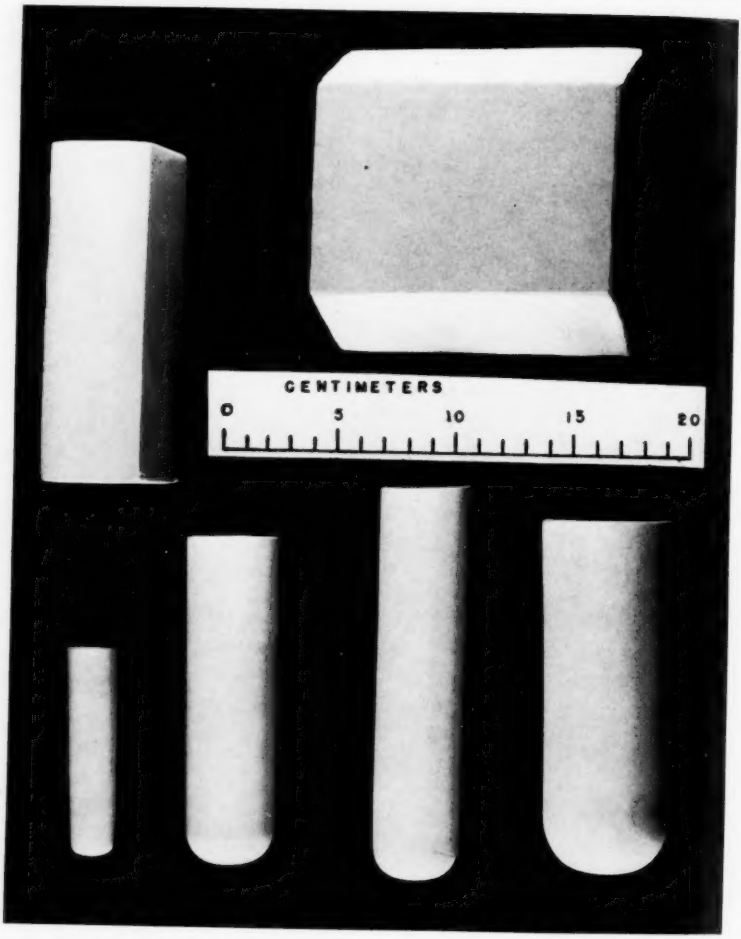

FIGURE 2.—*Specimens of crucibles and bricks prepared by slip-casting.*
The small crucible weighed 50 grams; the circle brick weighed 1,700 grams.

with increasing temperature of firing; but a maximum temperature of 1,750° or 1,800°C was used in our work, primarily to provide a safe margin for subsequent use of the crucibles at about 1,600°C rather than to produce a desired degree of porosity or density. Breakage of crucibles during firing was negligible when about 3 hours was required to reach the maximum temperature and this temperature was maintained for about 1 hour. After firing, the crucibles were white, hard, strong, and resistant to shock, with a structure similar to that of porcelain. If a suspended crucible was struck lightly, it responded with a clear, bell-like ring.

The split halves of the 3 crucibles that are shown in figure 1 illustrate the excellent inner surfaces and uniform walls that were attained in slip-cast crucibles. The largest of the 3 crucibles was 16 cm long with a capacity of 140 cm^3, the smallest was 9 cm long with a capacity of 20 $cm.^3$ The wall thickness of each of the three was 2.5 mm. In most of the crucibles the thickness of the bottom was the same as that of the walls; but the crucible shown at the left in figure 1 had a thick bottom, presumably because the bottom of the mold was dry and absorbed water from the slip faster than did the side walls. The largest slip-castings of beryllia that were attempted were crucibles 5 cm in inside diameter, 15 cm long, with walls 4 mm thick, and with a capacity of about 300 cm^3. One of these shells which were used to support smaller crucibles in melting operations is included in figure 2.

III. SLIP-CASTINGS OF ZIRCONIA, ZIRCON, ALUMINA, AND ELECTRICALLY FUSED THORIA

The success achieved in slip-casting beryllia led to experimentation with other refractories. No particular difficulty was encountered in slip-casting zirconia, zircon, or electrically fused thoria of the grades which had been previously used for the production of tamped or pressed crucibles [3]. However, some details of the procedure, for example, the time of grinding and the amount of water to make a suitable casting slip, necessarily were varied for different refractories. Electrically fused thoria required the longest grinding. Although crucibles made from this material did not shrink appreciably on drying in the mold, they were strong and heavy enough to permit their removal. The shrinkage of thoria crucibles on firing to 1,750° or 1,800° C was very low.

Alumina of satisfactory purity for use as a high-temperature refractory is a relatively new product. The best alumina that was previously available in this country was the purified oxide that was used for the production of metallic aluminum. The principal impurities in this material were sodium salts, equivalent to a content of about 0.5 percent of Na_2O, which lowered the sintering temperature of the alumina and increased its susceptibility to contamination by carbon. However, a special grade of purified alumina, "Grade A–10," is now available, the Na_2O content of which is about 0.1 percent and the other impurities are lesser amounts of the oxides of iron, silicon, and titanium.

The procedure employed in slip-casting crucibles of both grades of alumina was practically the same as was used for beryllia. The alumina as received had been calcined and was finely granulated, about 35 percent being retained on a No. 200 sieve. This material

was ground in a steel ball mill for 8 hours, treated with hydrochloric acid at room temperature for 24 hours, and washed with water for 24 hours. Crucibles made from alumina, which contained 0.5 percent of Na_2O, were sintered more than those made from A–10 alumina and fired at the same temperature. The increased sintering presumably resulted from the presence of sodium salts in spite of the treatment of the finely ground alumina with hydrochloric acid. Shrinkage of the alumina crucibles on firing to 1,750° C was about 15 percent, somewhat more than that of the beryllia; but the latter was calcined to 1,800° C, whereas the alumina was calcined at about 1,500° C.

The preparation of slip-cast crucibles of purified alumina, for use at high temperatures, has received more attention abroad than it has in this country and has been described in several papers in English journals [7, 8, 9]. Most of these procedures are more complicated and less convenient than ours. In some instances grinding for 100 hours was required; in several instances the treatment of the finely ground material with acid was done at temperatures that approached the boiling point of the mixture, or the slip was heated before it was cast. Our experiments indicated that satisfactory results were obtained with less than 10 hours' grinding and, further, that the entire process could be carried out at room temperature. These variations in detail are of minor importance, and all processes for slip-casting alumina are based on Ruff's discovery [6] that plasticity could be developed in nonplastic refractories by fine grinding and treatment with acid.

Brick for the construction of a small high-temperature furnace also were made from A–10 alumina by a modified slip-casting procedure. The alumina, not ground, did not develop a satisfactory bonding power when it was treated with diluted hydrochloric acid and washed with water. Brick formed from this material could be removed from the mold and were somewhat plastic while they were damp but lost their cohesion in drying and were converted to friable, sandy masses when they were heated to 150° C. On the other hand, alumina that had been ground for 8 or 10 hours in the ball mill and then treated with acid and water could be formed into brick that did not disintegrate when they were dried, but which, unfortunately, cracked badly. However, neither of these difficulties was encountered when a mixture of equal weights of unground alumina and of material that had been ground for 10 hours was used.

The procedure for casting the brick that were 5 cm thick differed in several respects from that used for the thin-walled crucibles, particularly in the thickness of the slip and in the type of mold. To form one brick of each of the two sizes illustrated in figure 2, 1,300 g of alumina that had been ground for 10 hours was mixed with 1,100 g of unground material. The mixture was treated with diluted hydrochloric acid for 24 hours and then was washed with water. After the mixture had stood overnight in a large evaporating dish, the water was siphoned off as completely as possible, and 200 g of dry unground Al_2O_3 was stirred into the mixture to form a pasty slip and to bring the composition to equal weights of ground and unground alumina. These slips contained 75 percent or more of solid matter.

Molds for the brick were without top or bottom and were made of wood. The surfaces of the mold that would be in contact with the slip were wrapped with strips of filter paper and the mold was then

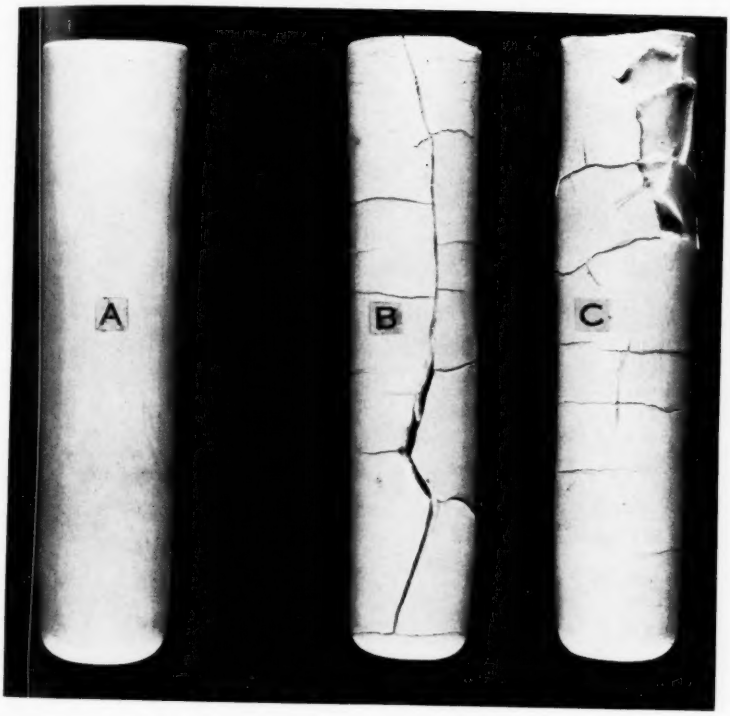

FIGURE 3.—*Slip-cast magnesia crucibles.*

Satisfactory crucibles, such as *A* were obtained from slips made with absolute alcohol. Crucibles *B* and *C* were cast from aqueous slips and cracked during firing.

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placed on a sheet of filter paper which in turn rested on a porous plate in a large funnel. The pasty slip was transferred to the mold by means of a large spatula or scoop, and each addition was puddled to fill the corners of the mold to insure complete mixing and to facilitate removal of air bubbles. After the mold was full, small additions of slip were made from time to time to compensate for the shrinkage, which was completed in about 2 hours. The casting was allowed to remain undisturbed in the mold for 2 or 3 hours more, the mold was then removed, the filter paper was stripped from the casting, and the latter was air dried for 36 hours. It was then baked at 150° C in an electric oven and subsequently was fired to about 1,425° C in one of the Bureau's kilns.[3] Some of the brick were fired to 900° C in an electric muffle, prior to firing to 1,425° C, but this intermediate firing was not an improvement over direct firing from the baked condition. In fact some of the brick were rather fragile after firing to 900° C, whereas there were no failures and no serious checks or cracks during the firing to 1,425° C. After baking at 150° C, the loss in weight of a 1,700-g brick on firing to 1,425° C did not exceed 5 or 10 g, and the linear shrinkage was only about 1 percent. Examples of two types of brick fired to 1,425° C are shown in figure 2. The circle brick were 5 cm thick, 14 by 9 cm at one face, and 14 by 14 cm at the other. The soaps were 5 cm square, 15 cm long, and weighed about 800 g each. The slip-cast articles shown in figure 2 vary in weight from 1,700 g for the circle brick to less than 50 g for the small crucible.

IV. SLIP-CAST MAGNESIA CRUCIBLES

The slip-casting of calcined ground magnesia presented unusual problems because of the tendency of this material to react with acids and even with water. Treatment of the ground material with diluted hydrochloric acid dissolved some of the magnesia and converted the rest to a hard, nonplastic mass. Various proportions of alcohol were added to the diluted hydrochloric acid in the hope that the reaction with the magnesia could be inhibited, but without success. It was concluded that the removal of iron, from grinding in the steel ball mill, was not practicable by treatment with diluted acid. Furthermore, the treatment with acid was not needed to develop plasticity in the magnesia; this material developed excessive plasticity from treatment with water. A few successful castings of magnesia were made from water slips, but many difficulties were encountered. The magnesia slip was sticky and rubbery as compared to slips of the other refractories, and the castings were soft and weak and stuck tightly to the mold. Of the few good castings that were successfully removed from the mold, none was satisfactorily dried and fired. All developed cracks and checks, as did the two crucibles shown at the right in figure 3. However, crucibles which cast well and which could be dried and fired without breakage, as exemplified by the crucible at the left of figure 3, finally were obtained through the use of a nonaqueous liquid to form the slip.

Magnesia crucibles were slip-cast successfully as follows: Magnesia that had been previously calcined to about 1,800° C was ground in a steel ball mill. Enough of the ground magnesia to make a 1

[3] The authors are indebted to R. A. Heindl and his associates in the Refractories Section of the Bureau for the use of the kiln and for information about ceramic slip-casting.

day's supply of castings was covered with an excess of absolute alcohol, and the mixture was shaken vigorously several times and then allowed to settle overnight. In the morning most of the supernatant liquid was siphoned off until only enough remained to convert the cake of magnesia into a fluid slip of the desired consistency when the mixture was shaken.

To obtain a stable suspension in alcohol, that is, one which did not settle rapidly, required longer grinding than was necessary for aqueous slips. Magnesia ground in the ball mill for 17 hours made a satisfactory slip with absolute alcohol. The casting slips contained 80 to 85 percent solid matter and were somewhat more viscous than the aqueous slips. It should be emphasized that the medium for successful slip-casting of magnesia was *absolute* alcohol. Slips made with 95-percent alcohol were no better than slips made with water alone.

Castings of magnesia formed rather slowly, dried rather slowly, and tended to stick to the mold. However, the green crucibles appeared to be quite tough and able to withstand the rather severe jolting of the mold that was usually necessary to free the castings. No difficulty was encountered in drying and firing the crucibles, although the magnesia, perhaps because it contained impurities that were removed from the other refractories by the treatment with acid, was not quite as refractory as the beryllia or purified alumina. When fired to 1,750° or 1,800° C the magnesia crucibles became somewhat vitrified and tended to warp out of shape. At 1,650° or 1,700° C they kept their shape but tended to vitrify more than did the other refractories at temperatures 100° C higher.

Absolute alcohol was the only successful vehicle for slip-casting magnesia that was found in our experiments, but equally good success perhaps could be attained with other nonaqueous, nonhydrating media.

V. SUMMARY

1. Beryllia crucibles with uniform thin walls, smooth inner surfaces, and with capacities up to 300 cm^3 were prepared by a slip-casting process.

2. The necessary plasticity for slip casting was developed in calcined, finely ground beryllia by treatment with diluted hydrochloric acid at room temperature.

3. Good castings were obtained from suspensions of the acid-treated beryllia in diluted hydrochloric acid, but equally good castings and longer life of the plaster molds were obtained when the diluted acid of the casting slip was replaced with water.

4. The slip-casting process that was developed for beryllia was also used for the preparation of crucibles of alumina, thoria, zircon, and zirconia.

5. Slip-cast crucibles had wall thicknesses of about 3 mm, but brick 5 cm in thickness were prepared by a modification of the slip-casting process.

6. Crucibles of magnesia, which could not be cast from aqueous slips, were cast from suspensions of magnesia in absolute alcohol.

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